

CANADIAN JOURNAL OF RESEARCH

VOLUME 13

JULY, 1935

NUMBER 1

CONTENTS

SEC. A.—PHYSICAL SCIENCES

	Page
The Spectrum of Trebly Ionized Cerium— <i>R. J. Lang</i> - - -	1
Measurement of Small Capacities in Terms of Mutual Induc- tance and Resistance— <i>W. H. Watson</i> - - - - -	5
Anomalous Dispersion of Sound in Solid Cylindrical Rods — <i>R. Ruedy</i> - - - - -	10
The Thermal Conductivity of Sundry Materials— <i>C. D. Niven</i> -	16

SEC. B.—CHEMICAL SCIENCES

The Sorption of Water Vapor on Cellulosic Materials— <i>Edgar Filby and O. Maass</i> - - - - -	1
The Hydrogenation of Alberta Coals. II. Comparative Data on Thirteen Coals of Various Ranks and Two Suspension Media, Tetralin and Liquid Petrolatum— <i>E. H. Boomer, A. W. Saddington and J. Edwards</i> - - - - -	11
Studies on Lignin and Related Compounds. XII. Methanol Lignin— <i>Fritz Brauns and Harold Hibbert</i> - - - - -	28
Studies on Lignin and Related Compounds. XIII. The Struc- ture and Properties of Glycol Lignin— <i>K. R. Gray, E. G. King, Fritz Brauns and Harold Hibbert</i> - - - - -	35
Studies on Lignin and Related Compounds. XIV. The Action of Lead Tetra-acetate and of Mercuric Acetate on Glycol Lignin Derivatives— <i>K. R. Gray, Fritz Brauns and Harold Hibbert</i>	48
Studies on Lignin and Related Compounds. XV. Phenol Glycol Lignin— <i>Fritz Brauns and Harold Hibbert</i> - - - - -	55

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

Publications and Subscriptions

The Canadian Journal of Research is issued monthly in four sections, as follows;

- A. Physical Sciences
- B. Chemical Sciences
- C. Botanical Sciences
- D. Zoological Sciences

For the present, Sections A and B are issued under a single cover, as also are Sections C and D, with separate pagination of the four sections, to permit separate binding, if desired.

Subscription rates, postage paid to any part of the world (effective 1 April, 1939), are as follows:

	<i>Annual</i>	<i>Single Copy</i>
A and B	\$ 2.50	\$ 0.50
C and D	2.50	0.50
Four sections, complete	4.00	—

The Canadian Journal of Research is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

National Research Council, Ottawa, Canada.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 13, SEC. A.

JULY, 1935

NUMBER 1

THE SPECTRUM OF TREBLY IONIZED CERIUM¹

By R. J. LANG²

Abstract

The spectrum of cerium has been photographed from $\lambda 3600$ to $\lambda 500 \text{ \AA}$ by means of a two-meter grating of 30,000 lines per inch mounted in a vacuum spectrograph, using the vacuum spark and the spark in nitrogen as sources. An analysis of the spectrum of Ce IV results in the location of the 6S-6P, 6P-6D, 6P-7S, 5D-6P, 6P-8S and possibly the 6P-7D multiplets. The ionization potential is approximately 33.3 volts.

Introduction

Virtually nothing is known concerning the single-electron spectrum of cerium although several attempts have been made to locate some of the doublets which are expected to occur in the spectral region below 3000 \AA . Gibbs and White (3) gave a pair of lines having a separation of 4620 cm^{-1} which were thought to represent the main doublet 6S-6P. Both lines were later changed by these authors (4) and another pair in the close neighborhood of the former was given showing a separation of 4707 cm^{-1} . This latter assignment was made independently by Badami (1) and is confirmed by the results here presented. However, the further analysis of the spectrum made by Badami does not correspond to the present work.

Experimental Procedure

The spectrum of cerium was photographed from $\lambda 3600$ to $\lambda 500 \text{ \AA}$ on a two-meter grating having 30,000 lines per inch mounted in a vacuum spectrograph, using the vacuum spark and the spark in an atmosphere of nitrogen as sources. In the latter case the electrodes were placed parallel to the slit so that the pole effect might be obtained. It is well known that as inductance is added to the circuit the radiations representing the higher spark spectra are confined more and more to the region of the tips of the electrodes and finally disappear. The source of energy used was a transformer giving a maximum of 30,000 volts with a condenser of small variable capacity across the secondary. Schumann plates were used entirely and the exposures ranged from ten minutes to three hours, depending on the region photographed and the kind of source used. Two small pieces of cerium metal which were of a rather high degree of purity were kindly supplied by Dr. Stover of the Chemistry Department of this university, and were used as electrodes.

¹ Manuscript received May 22, 1935.

Contribution from the Department of Physics, University of Alberta, Edmonton, Canada with financial assistance from the National Research Council of Canada.

² Professor of Physics, University of Alberta.

The spectrum is very rich in lines, as might be expected of an element in the position that cerium occupies in the atomic table, and it would be next to impossible to make any analysis without some means of separating the lines into the various stages of ionization.

Theoretical Analysis

After the spectrum had been photographed as stated above, the doublet suggested by Gibbs and White was examined carefully to make sure the lines really belong to Ce IV. This was clearly confirmed and the interval 4707 cm^{-1} was used throughout from $\lambda 2500 \text{ \AA}$ down to the limit of the spectrum photographed. This resulted in several pairs of lines, some of which seemed undoubtedly to be Ce IV lines. In particular the following three strong lines were outstanding on the plates of the vacuum spark:

1372.72 (75)	72,848.0
1332.16 (75)	75,066.0
1289.41 (50)	77,554.8

Fortunately, there are scarcely any other lines of comparable intensity in the neighborhood and certainly none of equal intensity. These three lines are clearly the 5D-6P multiplet. The relative intensity of the lines is characteristic of this multiplet in many similar spectra. The discovery of this multiplet was taken as strong confirmation of the reality of the 6S-6P doublet, and accordingly a fuller analysis of the spectrum was attempted on this basis.

TABLE I
THE SPECTRUM OF CE IV

Assignment	λ I.A.	Int.	Wave number	Interval	Config-uration	Term	Term value
6S ₁ -6P ₂	2456.86	45	40,690.1	4706.2	5p ⁴ 5d	³ D ₂	0.0
6S ₁ -6P ₁	2778.20	90	35,983.9			³ D ₃	2488.8
6P ₂ -6D ₂	2063.13	10	48,454.5	598.8	5p ⁴ 6s	³ S ₁	36,864.4
6P ₂ -6D ₃	2037.95	18	49,053.3	4707.3		³ P ₁	72,848.0
6P ₁ -6D ₂	1881.05	18	53,161.8		5p ⁴ 6p	³ P ₂	77,554.8
6P ₂ -7S ₁	1779.03	20	56,210.4	4706.5	5p ⁴ 6d	³ D ₂	126,009.6
6P ₁ -7S ₁	1641.58	15	60,916.9			³ D ₃	126,608.1
5D ₂ -6P ₁	1372.72	75	72,848.0	4706.8	5p ⁴ 7s	³ S ₁	133,765.0
5D ₃ -6P ₁	1332.16	75	75,066.0			2488.8	
5D ₃ -6P ₂	1289.41	50	77,554.8		5p ⁴ 8s	³ S ₁	182,895
6P ₂ -8S ₁	949.30	3	105,341	4706	5p ⁴ 7d	³ D ₂	183,996
6P ₁ -8S ₁	908.70	1	110,047			³ D ₃	184,219
6P ₂ -7D ₂	939.49	1	106,441	223			
6P ₂ -7D ₃	937.52	3	106,664	4706			
6P ₁ -7D ₃	899.71	3	111,147				

Table I shows the classified lines of Ce IV together with the wave numbers and intervals. The last column shows the term values measured upward from the deepest term $5D_2$ which has been given zero value. The values of the inner quantum number j have been increased by $\frac{1}{2}$ to facilitate the printing of the report. The intensities are taken from plates of the vacuum spark spectrum. The confirmation of these assignments, aside from the question of equal intervals, is sought in the regular doublet law and the Moseley law. The results of the application of the regular doublet law, which has to do with the relation of intervals throughout an isoelectronic sequence of ions, are given in Table II. Cs I (2), Ba II(7) and La III(8), together with Ce IV, form such a sequence in which the spectrum arises from a single valence electron, a so-called stripped atom sequence in which each structure corresponds to a simple doublet spectrum. The table shows the screening constants s for the intervals $\Delta\nu$ for the $5D$, $6P$ and $6D$ terms. It is evident from the table that the screening constants decrease in a normal fashion which one is led to expect from many other similar sequences.

TABLE II
THE REGULAR DOUBLET LAW

	$\Delta\nu$	Z	$(\frac{\Delta\nu}{K})^{\frac{1}{2}}$	s
(5D ₂ -5D ₃)				
Cs I	98	55	10.60	44.40
Ba II	801	56	17.92	38.08
La III	1603	57	21.31	35.69
Ce IV	2489	58	23.79	34.21
(6P ₁ -6P ₃)				
Cs I	554	55	14.23	40.77
Ba II	1691	56	18.81	37.19
La III	3096	57	21.88	35.12
Ce IV	4707	58	24.30	33.70
(6D ₂ -6D ₃)				
Cs I	43	55	9.89	45.11
Ba II	205	56	14.61	41.39
La III	434	57	17.62	39.38
Ce IV	599	58	19.10	38.90

TABLE III
THE MOSELEY LAW VALUES OF $\sqrt{\frac{\nu}{R}}$ AND DIFFERENCES

	Cs I	Δ	Ba II	Δ	La III	Δ	Ce IV
5D ₂	0.391	0.436	0.827	0.380	1.207	0.353	1.560
6S ₁	0.535	0.322	0.857	0.304	1.161	0.295	1.456
6P ₂	0.423	0.308	0.731	0.299	1.030	0.293	1.323
6D ₂	0.283	0.278	0.561	0.286	0.847	0.294	1.141
7S ₁	0.343	0.248	0.591	0.249	0.850	0.262	1.112
8S ₁	0.254	0.200	0.454	0.207	0.661	0.227	0.888

In Table III the Moseley law has been applied to the corresponding term values throughout the same sequence. The differences are seen to be about as regular as those for the preceding row of similar structures (5) in the atomic table.

The few F terms in this sequence which are known appear highly irregular. In Cs I the 4F terms are unresolved because the combination with 5D falls in the infra-red, and the 5F terms are inverted and very narrow. In Ba II

none of the three known F terms are inverted but all have virtually the same separation of about 225 cm^{-1} . In La III no F terms were discovered and it was suggested that the $5D-4F$ combination in this spectrum might lie in the infra-red, but an investigation as far as $\lambda 10,500 \text{ \AA}$ failed to reveal the lines (8). The author, who had been working independently on La III, found this combination in the ultraviolet:

$5D_2-4F_3$	1081.61(15)	92,454.7	
			1603.4
$5D_3-4F_4$	1099.73(15)	90,931.4	
			80.1
$5D_3-4F_3$	1100.70(7)	90,851.3	

These lines are isolated and outstanding on the vacuum spark plates and there seems no doubt of their correctness.

It does not seem possible to locate the corresponding $5D-4F$ multiplet in Ce IV without ambiguity on the author's vacuum spark plates. It would be expected about 650 \AA but while there are several prominent lines near this value it may be that the satellite is missing. This is unfortunate because of the interest in deciding whether the first electron bound to the stripped atom is $5d$ or $4f$. It seems at present that there must be something erroneous about the F terms of Ba II and these should be carefully investigated again.

The $6P-8S$ doublet in La III has also been located:

$6P_2-8S_1$	1399.01	(2)	71,480
$6P_1-8S_1$	1462.26	(5)	68,387

The ionization potential can be found approximately for the Ce IV ion. There are three S terms available and at least two D terms. The $6P-7D$ multiplet is not very certain and the $7d^2D$ term is therefore probably doubtful. Simply by using a Rydberg table, and having in mind the sequence of term values in Table III, the value of the deepest term is approximately $269,500 \text{ cm}^{-1}$ which corresponds to an ionization potential of 33.3 volts compared with 33.8 volts for Zr IV (5). A similar close agreement is found for Yt III(6) and La III(8) both of which give a value close to 20 volts. It should be stated that the term values for La III on which Table III is based are about 4% greater than those given by Russell and Meggers, in order to make the run of values for the Moseley law as uniform as possible.

Acknowledgment

The author wishes to thank Dr. Stover for the cerium metal.

References

1. BADAMI, J. S. Proc. Phys. Soc. 43 : 53-58. 1931.
2. FOWLER, A. Series in line spectra. Fleetway Press, Ltd. London. 1922.
3. GIBBS, R. C. and WHITE, H. E. Proc. Natl. Acad. Sci. 12 : 551-555. 1926.
4. GIBBS, R. C. and WHITE, H. E. Phys. Rev. 33 : 157-162. 1929.
5. KIESS, C. C. and LANG, R. J. Bur. Standards J. Research, 5 : 305-324. 1930.
6. MEGGERS, W. F. and RUSSELL, H. N. Bur. Standards J. Research, 2 : 733-769. 1929.
7. PASCHEN, F. and GÖTZE, R. Seriengesetze der Linienspektren. J. Springer, Berlin. 1922.
8. RUSSELL, H. N. and MEGGERS, W. F. Bur. Standards J. Research, 9 : 625-668. 1932.

MEASUREMENT OF SMALL CAPACITIES IN TERMS OF MUTUAL INDUCTANCE AND RESISTANCE¹

BY W. H. WATSON²

Abstract

Campbell's a-c. bridge for the measurement of self-inductance in terms of mutual inductance can be modified so as to measure small capacities (1–1000 $\mu\text{mf.}$). The arrangement described is sensitive to within 0.01 $\mu\text{mf.}$ Small condensers can be measured to within 1% with ease. Residual errors are discussed.

The method described here for measuring small capacities suggested itself from an observation in the course of an exercise with Campbell's bridge for the measurement of self-inductance in terms of mutual inductance (1, p. 298). It was found that when a resistance of a few thousand ohms was joined between the source and the secondary of the mutual inductance, M , the value of M for balance instead of being zero as expected, turned out to be about 0.1 mh. Inspection of the disposition of the circuit made it reasonable to suppose that this disturbance of the normal condition of balance was due to capacity in the position indicated by C in Fig. 1. This hypothesis was soon justified by calculation and by subsequent measurements in which a known capacity was used, and the apparatus arranged so as to reduce stray capacity. It was recognized that this circuit offers a sensitive means of measuring small capacities which it is convenient to use whenever Campbell's variable standard and balancing inductance are available.

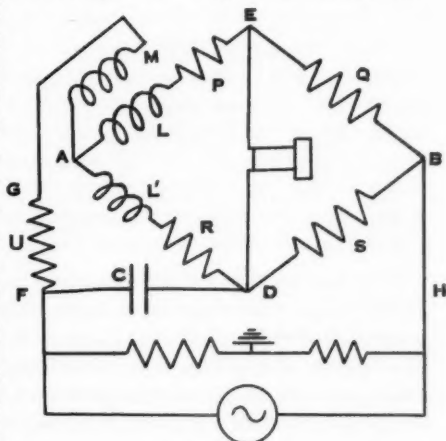


FIG. 1.

If l_1 denotes the effective inductance between F and A , and U the total resistance, and the other quantities are as indicated in the figure, then it can readily be established by a double transformation of the network (1, p. 47) that the following are the conditions for no current through the detector when the source supplies an e.m.f. of angular velocity p :

$$L' \frac{Q}{S} - L + M \left(\frac{Q}{S} + l_1 \right) = C \{ U(P+R) + RP - p^2[(L+L')l_1 + LL' - 2ML' - M^2] \} \quad (1)$$

and

$$\frac{QR}{S} = P - p^2 C \{ (U+R)(L-M) + P(l_1+L') + U(L'+M) + R(l_1-M) \} \quad (2)$$

¹ Manuscript received May 17, 1935.

Contribution from the Department of Physics, McGill University, Montreal, Quebec, Canada.

² Assistant Professor of Physics, McGill University.

The conditions of balance are dependent on the a-c. frequency employed, but if C is small, U has to be made large for sensitivity, so that, when L' is the proper balancing coil for the primary of M , Condition (1) becomes approximately:

$$M\left(\frac{Q}{S} + 1\right) = CU(P + R) \quad (3)$$

and in any case the frequency need not be known very accurately if a more precise measurement is required.

The method of measurement is to make a preliminary test of Campbell's bridge with U and C absent. M should be equal to zero or very nearly so. U is then introduced and the bridge balanced with the condenser C out of circuit, but with the leads to it in position. Only a very small change in M and P should be required when this arrangement is made; if this is not the case, there is probably stray capacity between U and some part of the bridge. The condenser is next connected and M and P adjusted for balance; for a small capacity, the change in P will not be great but will depend on the frequency, while the change in M can be made to have any desirable value by the proper choice of Q/S and U . With an equal ratio bridge the well known advantages with respect to residuals in the ratio arms are secured, but as the balancing coil L' is usually supplied for $Q/S = 9$ it is convenient to use this, and it is possible to measure easily, within 1%, capacities of a few micromicrofarads. A further advantage of the ratio 9:1 is that it makes U larger and the bridge therefore more sensitive for the measurement of C , while, as a less important consequence, the large value of U renders the approximate formula (Equation (3)) applicable for routine work.

Provided that a suitable source and detector are available, there is no difficulty in establishing an accurate balance of the bridge which can be made sensitive to within $0.01 \mu\mu\text{f.}$, but it is obvious that such a bridge may also be seriously affected by residuals in the resistance boxes and other apparatus employed, and in the actual arrangement of the apparatus and connections. By far the most important sources of error due to residuals arise from neglect of the residual capacity of the resistance U , and from the presence of appreciable capacity between G and D . The latter can be kept small, if care is taken in setting up the bridge, its presence being clearly demonstrated if P has to be altered very much when U is introduced into the circuit. It can be easily shown that capacity between G and D produces changes in the effective values of U and C which, however, are not serious because they leave the product CU unaltered. In addition, however, it may make a large negative contribution to l_1 and this also is the effect of the self-capacity of U . For, if U is shunted by a small capacity k , the impedance operator is $U - jpkU^2$ (kU being small); there is therefore a contribution $-kU^2$ to l_1 . Provided that P is not small—a condition which is desirable on other grounds—the effect of l_1 in Equation (1) will generally be negligible, if 1% accuracy is all that is required. On the other hand, the effect of l_1 in Equation (2) will always be important, and may lead to a decrease in P when C is introduced.

Impurity in the mutual inductance will enter as a correction to P which becomes of less importance the greater P is. P cannot be made greater than about 1000 ohms without introducing error due to its self-capacity. If the condenser is an impure one with effective series resistance ρ , the term $QR\rho C/S$ enters Equation (1) and is obviously quite negligible. Residual inductance in the ratio arms is of importance only in the second condition of balance (Equation (2)).

When it is required to measure a condenser of capacity less than $1000 \mu\text{f}$. by this method, the suitable values to be given to P , R , Q , S are fairly well determined by the above considerations. The writer has, however, investigated the effects of varying p , U , R and Q , and the influence of a small capacity shunting Q or U , and found that, provided that the apparatus is well arranged so as to reduce capacity between the arms of the network, consistent measurements of C can be obtained, even if these variables are not kept within narrow limits.

Some sample measurements are given in Table I. A valve oscillator supplying a.c. of 806.3 cycles per second was coupled by a step-up transformer to an earthing device (1, p. 368) and from that to the bridge by means of shielded cable. As detector, telephones were used with an amplifier giving a 1000 : 1 gain, coupled through a shielded transformer to the bridge. Two condensers were measured; one was a General Radio Type 222 precision condenser, with the maker's calibration available, the other was a variable cylindrical condenser whose capacity was calculated from geometrical data. As a matter of interest, the grid-plate capacity of a triode 201A was measured and found to be $10.1 \mu\text{f}$.

The results given in Table I indicate how well the mutual inductance can be set and the satisfactory agreement between the measured values of C and the data of the maker. Neglect of PR and l_1 in Equation (1) leave the values of C obtained by means of Equation (3) not more than 4 parts in error per 1000. There is no reason why one should not attempt to evaluate these corrections if higher accuracy is required, but, of course, the amount of work involved is very much greater. In the fifth column of Table I the quantity $(SP - RQ)/SC$ is given; according to Equation (2) it should be a constant and if U had no self-capacity, would yield the value of $U(L + L')p^2$, and hence $L + L'$. The result is 19.2 mh., which is to be compared with the known value 24.8 mh. If this large difference were due entirely to the residual capacity of U , the capacity in question would have to be $56 \mu\text{f}$. or the effective inductance l_1 would have to be -0.56 h . In order to check this, U was connected to a balanced Schering condenser bridge (1, p. 242) in parallel with the arm S of 2000 ohms. The capacity shunting S was found to be $56.2 \mu\text{f}$. This is an excellent agreement, for the other residuals already discussed could account only for a small part of the difference $24.8 - 19.2 \text{ mh}$. referred to.

In the above-mentioned experiments the error introduced in the value of C due to neglect of the effect of the residual capacity of U on its effective

resistance $U(1 + p^2 k^2 U^2)^{-1}$ is only 0.06%. One should not however overlook the fact that a serious error may arise from this source if p or k happens to be larger. Attention has been drawn by Jones and Josephs (2) to the errors in high resistances caused in this way. It is important to notice that in other bridges for measuring small capacities and depending on the use of a high resistance, this residual must be kept in mind, and it is perhaps not out of place to mention that in a discussion of residuals in Anderson's bridge, Hague (1, p. 261) omits this effect in r .

TABLE I

(a) G.R. Type 222 condenser

C (maker), $\mu\text{mf.}$	M , $\mu\text{h.}$	P , ohms	C , Eqn. (3), $\mu\text{mf.}$	$\frac{SP - RQ}{SC} \times 10^{-10}$
Out of circuit	3	921.1	0.3	—
48	496	923.4	48.3	4.79
98	1003	925.9	97.7	4.90
217	2242	931.8	216.7	4.93
340	3543	937.9	340.6	4.94
466	4881	944.1	466.4	4.89
593	6247	950.4	593.3	4.94
782	8317	959.4	783.3	4.90
1028	11,063	971.9	1029	4.94

(b) Cylindrical condenser

Condenser scale reading, cm.	M , $\mu\text{h.}$	P , ohms	C , $\mu\text{mf.}$	Differences, $\mu\text{mf.}$	$\frac{\mu\text{mf.}}{\text{cm.}}$
3.00	172	921.2	16.77		
8.00	265	921.6	25.87	9.10	1.82
10.00	302.5	921.8	29.54	12.77	1.82
13.00	359	922.1	35.04	18.27	1.83

Frequency = 806.3 cycles/sec. $Q/S = 900/100$; $U = 100,000$ ohms. The maximum resistance and self-inductance of the secondary of M are 10 ohms and 9 $\mu\text{h.}$ respectively. $R = 102.4$ ohms.

The calculated value of the capacity per cm. of the coaxial cylinder was 1.85 $\mu\text{mf./cm.}$ (first approximation).

It was suggested to the writer by Dr. H. G. I. Watson that the places of U and C in the network might be changed, with advantage, to the following:— U between B and H and C between D and H . With this arrangement which is practically the conjugate network to Anderson's bridge, the conditions of balance are

$$-M \left(\frac{Q}{S} + 1 \right) = C \left\{ RU \left(\frac{Q}{S} + 1 \right) + RQ - p^2 (L' + M) l_1 \frac{Q}{S} \right\} \quad (4)$$

and

$$= \frac{QR}{S} - p^2 C \left\{ l_1 \left(\frac{Q}{S} + 1 \right) R + (L' + M) \left[\left(\frac{Q}{S} + 1 \right) U + Q \right] \right\}. \quad (5)$$

If l_1 were zero, then Condition (4) would be independent of the frequency, but as l_1 is quite large the arrangement can be quite inaccurate for measuring any but the smallest condensers unless an equal ratio bridge is used. Even when $Q/S = 1$, the error introduced by neglect of l_1 in determining C may be larger than with U and C on the other side of the bridge, on account of the fact that l_1 is multiplied by M^* . This objection would also apply in a slightly modified form to the use of the Campbell-Heaviside equal ratio bridge. These conclusions are supported by experiment.

Acknowledgment

The writer is indebted to Dr. H. G. I. Watson for helpful discussion and for assistance in some of the measurements.

References

1. HAGUE, B. Alternating current bridge methods. 2nd ed. Sir Isaac Pitman and Sons, Ltd. London. 1930.
2. JONES, G. and JOSEPHS, R. C. J. Am. Chem. Soc. 50 : 1049-1092. 1928.

**Provided that the effective self-inductance due to the residual capacity of U were balanced out by the inclusion of an equal self-inductance in series with U , this arrangement would be far more convenient, because P , which is adjusted for balance, does not appear in Equation (4), and then if $R = 100$ ohms, $U = 10^8$ ohms, the mutual inductance would give C directly as $M/10 \mu\text{f.}$, M being in $\mu\text{h.}$*

ANOMALOUS DISPERSION OF SOUND IN SOLID CYLINDRICAL RODS¹

By R. RUEDY²

Abstract

The deviation of the overtones from whole multiples of the fundamental note when pure longitudinal waves are set up in a cylindrical rod, one to a few centimetres in thickness, is accounted for to within less than 1% by the drop in the velocity of propagation of longitudinal waves with increasing frequency due to radial motion in the rod. The radial component present in vibrating solid or hollow cylinders determines a second solution of the velocity equation which starts near the resonance frequency of the radial vibration. Although radial motion can take place free from longitudinal components, so that no mutual coupling need exist between the two types of vibration, the equation for thin rods can within certain frequency ranges be reduced to the frequency relations valid for coupled systems.

Introduction

The velocity of propagation, c , of longitudinal waves of sound of frequency f , in a solid cylindrical rod of radius a , is given by the formula.

$$1 - \frac{c^2}{c_0^2} \frac{m+1}{m} = \frac{1 - \frac{ka J_0(ka)}{J_1(ka)}}{1 - \frac{\frac{c^2}{c_0^2} \frac{(m+1)}{m} - 1}{\frac{c^2}{c_0^2} \frac{(m-2)(m+1)}{(m-1)m} - 1} \frac{h_1 a J_0(h_1 a)}{J_1(h_1 a)}}$$

where

m = the reciprocal of Poisson's ratio μ

c_0 = velocity of sound at low frequencies

$$k = \frac{2\pi}{c/c_0} \frac{f}{c_0} \sqrt{\frac{2(m+1)}{m} \frac{c^2}{c_0^2} - 1}$$

$$h_1 = \frac{2\pi}{c/c_0} \frac{f}{c_0} \sqrt{\frac{(m-2)(m+1)}{(m-1)m} \frac{c^2}{c_0^2} - 1}$$

As long as c^2/c_0^2 is smaller than $(m-1)m/(m+1)$ ($m-2$), h_1 is an imaginary quantity ih .

TABLE I

OBSERVED AND COMPUTED VELOCITIES OF SOUND IN
CYLINDRICAL RODS OF NICKEL

Frequency, kc. per sec.	Velocity, c/c_0	f/c_0 , observed	f/c_0 , calcd.
188.7	0.9526	0.381	0.381
226.9	0.9164	0.458	0.459
242.8	0.8913	0.490	0.492
256.5	0.8631	0.518	0.525
270.1	0.8391	0.545	0.547

Length of rod, 100 mm.; diameter, 10 mm.; $m = 3.25$,
 $c_0 = 4952$ m. per sec.

With the usual values of m , the velocity decreases first slowly from c_0 to about $0.9c_0$, reached near the frequency $c_0/4a$, and then drops more rapidly to about $0.6c_0$ near the frequency $0.4c_0/a$, where an apparent discontinuity occurs. How well the theory agrees with the measurements is shown in Table I for

¹ Manuscript received May 17, 1935.

Contribution from the Division of Research Information, National Research Laboratories, Ottawa, Canada.

² Research Investigator, National Research Laboratories, Ottawa.

nickel rods and in Figs. 1 and 2 for thin steel, aluminium and copper rods through which sound, in some cases, of nearly one million cycles per second, was sent (3, 5). Since the velocity depends merely on the product fa , and not on f and a separately, the results have been calculated on the

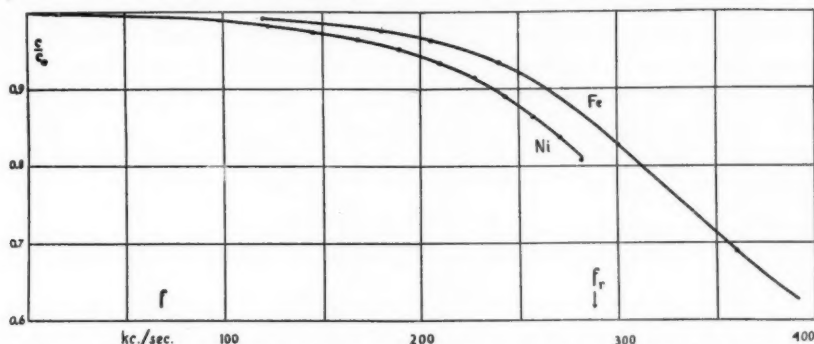


FIG. 1. Velocity of sound as a function of the frequency, f , for cylindrical rods of nickel and steel, 1 cm. thick. The curves represent theoretical values, the dots observed ratio of the velocity, c , to the velocity c_0 , at low frequencies (3).

basis of a diameter of 1 cm., which is the thickness of the nickel rod. The normal values of Poisson's ratio for nickel (0.31) and steel (0.29) have been adopted, with no attempt to improve the results by adjusting this ratio which differs slightly from rod to rod, depending on the history of the sample. The ratios adopted for aluminium and copper are lower than normal, 0.31 in place of 0.33, but the rods are vibrating in air, and the damping thus introduced tends to lower the natural frequency of thin rods.

According to the theory, in materials having the same number m , the velocity c/c_0 varies in the same way, providing that it be plotted as a function of f/c_0 . Fig. 2 illustrates this point for aluminium and copper; the data obtained for both metals fall upon the same curve.

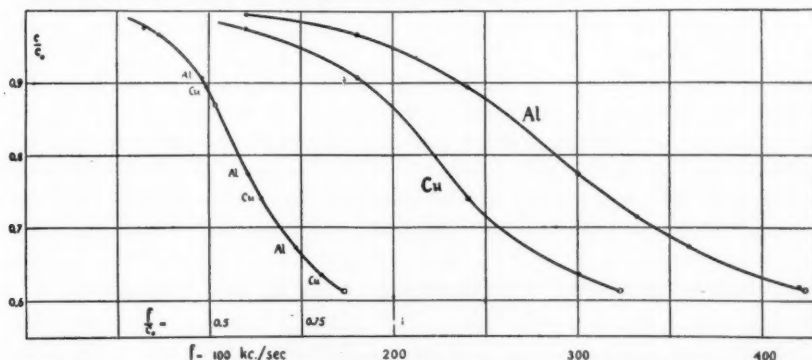


FIG. 2. Velocity of sound, as a function of the frequency, for cylindrical rods of copper and aluminium, 1 cm. thick (3). The circles represent computed, the black dots observed, values. At the left the results are plotted as a function of f/c_0 , using 0.32 as Poisson's ratio; lower values of this ratio shift the curve slightly to the right.

The measured velocities refer to standing rather than progressive waves. Since the rigorous solution for standing waves does not result in a purely periodic function of the radial and longitudinal motion taken separately, a correction would have to be applied to the observed velocities. In the case of the rods in question, all less than one centimetre thick, the end effects are negligible and the correction may be disregarded. For thicker rods standing waves can no longer be represented as the result of two longitudinal waves progressing in opposite directions.

For velocities smaller than c_0 , the displacements u , in the direction of the radius, and w , in the direction of the axis of the rod, are for any position, z , along the axis given by

$$u = \gamma J_1(ka) \left(\frac{J_1(kr)}{J_1(ka)} - \left(1 - \frac{c^2}{c_0^2} \frac{m+1}{m} \right) \frac{J_1(ihr)}{J_1(iha)} \right) e^{i(\gamma z + pt)}$$

$$w = \left(ka \frac{J_0(kr)}{J_1(ka)} + \frac{\frac{c^2}{c_0^2} \frac{m+1}{m} - 1}{\frac{c^2}{c_0^2} \frac{(m-2)(m+1)}{(m-1)m} - 1} \frac{ha J_0(ihr)}{i J_1(iha)} \right) \frac{i J_1(ka)}{a} e^{i(\gamma z + pt)}$$

or, at the surface of the rod, by

$$u = 2\pi \frac{f}{c} \frac{m+1}{m} \frac{c^2}{c_0^2} J_1(ka) e^{i(\gamma z + pt)}$$

$$w = \left(1 + \frac{\frac{c^2}{c_0^2} \frac{(m+1)}{m} - 1}{\frac{c^2}{c_0^2} \frac{(m-2)(m+1)}{(m-1)m} - 1} \frac{ha J_0(iha)}{i J_1(iha)} - \left(1 - ka \frac{J_0(ka)}{J_1(ka)} \right) \right) i \frac{J_1(ka)}{a} e^{i(\gamma z + pt)}$$

apart from a constant factor C , which is given by the initial conditions and which may be made equal to unity by a suitable choice of the units in which u and w are measured. When applying the formulas, the function

$$e^{i(\gamma z + pt)} = \cos(\gamma z + pt) + i \sin(\gamma z + pt)$$

is split up so as to render u and w real, whether $J_1(kr)$ be real or imaginary. However, as k approaches zero, the displacements at the surface ($r = a$) vanish; the rod appears motionless, and the common methods of measuring the velocity of sound fail in this range. For solutions with still smaller values of c/c_0 , and imaginary values of k , the displacements u and w would grow beyond any limit as the frequency is increased, so that it seems legitimate to reject solutions with imaginary values of k on the ground that they lead to a contradiction with the assumptions on which the velocity formula is based. Attempts to study the propagation of sound waves in this region have thus far met with failure despite the use of powerful sources of vibration (5).

Velocities at Higher Frequencies and Anomalous Dispersion

Although it seems difficult, on account of the small amplitude, to follow the propagation of frequencies higher than about $0.45 c_0/a$ through solid rods, the curve representing c/c_0 as a function of f/c_0 resembles, near this point, the curves representing anomalous dispersion, so that it seems worth while to

ascertain the value of f/c_0 for very high values of c/c_0 . In this case the equation giving the velocity of sound becomes

$$-\frac{c^2}{c_0^2} \frac{m+1}{m} = \frac{1 - la \frac{J_0(la)}{J_1(la)}}{1 - \frac{m-1}{m-2} ga \frac{J_0(ga)}{J_1(ga)}} \quad \text{for } \frac{c}{c_0} \gg 1,$$

where now, with $la < 1.841$ and $\gamma = 0$,

$$l = 2\pi \frac{f}{c_0} \sqrt{\frac{2(m+1)}{m}} \quad g = 2\pi \frac{f}{c_0} \sqrt{\frac{(m-2)(m+1)}{(m-1)m}}$$

$$3 > \frac{l}{g} = \sqrt{\frac{2(m-1)}{m-2}} > 1$$

The right-hand side of the equation becomes very large when

$$\frac{m-2}{m-1} = ga \frac{J_0(ga)}{J_1(ga)}.$$

This relation, however, represents but the resonance condition for pure radial waves along the rod. A kind of anomalous dispersion is of course to be expected in solid, as well as in hollow, rods. The values of ga satisfying the equation are given in Table II.

TABLE II
SOLUTIONS OF THE EQUATION $(m-2)J_1(ga) = (m-1)gaJ_2(ga)$

m	$(ga)_1$	$(ga)_2$	$(ga)_3$	l/g	μ	Material
2.22	2.325	5.483			0.45	Lead
2.50	2.254	5.451		2.45	0.40	Gold
3.00	2.166	5.428	8.595	2.00	0.33	Aluminium
3.33	2.126	5.414		1.87	0.30	Nickel
4.00	2.069	5.396	8.576	1.73	0.25	Glass

The frequency, f_r , at which the velocity tends to infinity, is obtained from

$$\frac{f_r}{c_0} = \frac{(ga)}{2\pi a} \sqrt{\frac{m(m-1)}{(m+1)(m-2)}}.$$

For $m = 3.25$ the value of f_r/c_0 is 0.76, so that the radial resonance frequency of a long rod is higher than the radial resonance frequency of a thin circular disc (1). However, in so far as it involves extremely high velocities of propagation, the computed resonance frequency is probably higher than the actual value. Oscillations which appear to form the radial resonance system have been observed at 287.5 kc. per sec. for a nickel rod, that is, when f/c_0 is equal to about 0.58, instead of at 330 kc. per sec.

Close to the radial resonance frequency, f_r , small changes in f/c_0 bring the velocity back to normal values, so that h and k must again be used in place of g and l . Near $c/c_0 = 1$ the velocity drops more slowly as the frequency is further increased, the ratio c/c_0 reaching the value $(m/(m+1))^{1/2}$ for

$ka = 5.33$, when $m = 3.5$ and f/c_0 is equal to about 1.5. The condition for a second region of radial resonance (near $f/c_0 = 2$ for $m = 3.25$) is then approached; but for these high frequencies the size of the grains making up the metal must make itself felt. In the descending branch of the curve the velocity remains greater than the value c for which $c^2/c_0^2 = m/2(m+1)$ and k is equal to zero since only one solution f exists for this point (4).

Resonance Frequencies in Rods and Frequencies in Coupled Systems

For the use of rods as frequency standards, a simple formula is desirable. Since in the range that is of practical interest, ha and ka for a rod 1 cm. in diameter are smaller than about four and as long as the diameter is small compared with the wave-length, the Bessel functions occurring in the velocity equation may be replaced by the first few terms of their development in series:

$$J_0(ha) = 1 - \frac{h^2 a^2}{4} + \frac{h^4 a^4}{64} - \frac{h^6 a^6}{2304} + \dots$$

$$J_1(ha) = \frac{ha}{2} \left(1 - \frac{h^2 a^2}{8} + \frac{h^4 a^4}{192} - \frac{h^6 a^6}{9216} + \dots \right).$$

Moreover, putting

$$e^2 = 1 - \frac{c^2}{c_0^2} \frac{m+1}{m} = 1 - \frac{c^2}{c_0^2} (1 + \mu)$$

$$h = 2\pi \frac{f}{c} H,$$

and retaining terms in $(ha)^4$ and $(ka)^4$ only, the equation becomes, outside the region of radial resonance,

$$\frac{a^4}{192} \left((h^2 - k^2)^2 \left(1 + e^2 + \frac{2e^4}{H^2} \right) + 4k^4 + 7h^2 k^2 + h^2 k^2 \left(\frac{8e^4}{H^2} + e^2 - 7 \right) \right) - \frac{a^2}{8} \left((h^2 - k^2) \left(1 + e^2 + \frac{2e^4}{H^2} \right) - 2k^2 + 2e^4 \frac{h^2}{H^2} \right) + \left(1 + e^2 + \frac{2e^4}{H^2} \right) = 0,$$

where

$$1 + e^2 + \frac{2e^4}{H^2} = \frac{c^2}{H^2 c_0^2} \left(1 - \frac{c^2}{c_0^2} \right) \frac{(m+1)^2}{m(m-1)}.$$

If the last term only is considered, the solution leads to a constant value $c = c_0$. The last two terms give

$$\frac{c^4}{c_0^4} + \frac{c^2}{c_0^2} \frac{\frac{8c_0^2}{a^2 p^2} - 7 + \frac{2\mu^2}{1-\mu}}{(1+\mu) \left(4(1-\mu) + \frac{1-2\mu}{1-\mu} \right) - \frac{8c_0^2}{a^2 p^2}} + \frac{2}{(1+\mu) \left(4(1-\mu) + \frac{1-2\mu}{1-\mu} \right) - \frac{8c_0^2}{a^2 p^2}} = 0.$$

When the assumption is made that $c^2/c_0^2 = 1 + \eta a^2$, and $8c_0^2/a^2 p^2$ is replaced by $8c_0^2/a^2 c^2 \gamma^2$, the well-known formula

$$\frac{c}{c_0} = 1 - \frac{\mu^2 a^2 \gamma^2}{4}$$

is obtained.

Considering that for standing waves, n being a whole number

$$p = 2\pi f = n\pi \frac{c}{L},$$

with sufficient accuracy for thin rods of length L ,

$$\frac{c^4}{c_0^4} - \frac{c^2}{c_0^2} \frac{\frac{8L^2}{n^2\pi^2a^2} + 7 - \frac{2\mu^2}{1-\mu}}{(1+\mu)(5-4\mu-\frac{\mu}{1-\mu})} + \frac{\frac{8L^2}{n^2\pi^2a^2} + 2}{(1+\mu)(5-4\mu-\frac{\mu}{1-\mu})} = 0,$$

or approximately

$$\frac{c^4}{c_0^4} - \frac{c^2}{c_0^2} \frac{\frac{4L^2}{n^2\pi^2a^2} + \frac{7}{2} - \frac{\mu^2}{1-\mu}}{\frac{5}{2}(1-\mu^2)} + \frac{\frac{4L^2}{n^2\pi^2a^2} + 1}{\frac{5}{2}(1-\mu^2)} = 0.$$

On the other hand, when the rod is considered as a system in which the longitudinal vibrations are mechanically coupled with the radial vibrations of thin sections, for which the resonance frequency is given by

$$f_0 = \frac{\xi c_0}{2\pi a} \sqrt{1-\mu^2},$$

where ξ is the solution of the equation for radial oscillations of thin discs,

$$\xi \frac{J_0(\xi)}{J_1(\xi)} = 1 - \mu,$$

and is closely equal to 2, then (1)

$$\frac{c^4}{c_0^4} - \frac{c^2}{c_0^2} \frac{\frac{\xi^2 L^2}{n^2\pi^2a^2} + (1-\mu^2)}{\frac{1-2\mu}{(1-\mu)^2} (1-\mu^2)^{\frac{3}{2}}} + \frac{\frac{\xi^2 L^2}{n^2\pi^2a^2}}{\frac{1-2\mu}{(1-\mu)^2} (1-\mu^2)^{\frac{3}{2}}} = 0.$$

There is a certain resemblance between the two equations, which explains why over a certain range the theory of coupled vibrations is capable of representing the results with great accuracy, though it fails completely as a general expression. The formula based on the velocity equation, on the other hand, is valid whenever longitudinal oscillations exist alone in thin rods, while flexural vibrations, or in the case of thicker rods, vibrations characteristic of plates, are absent. Both formulas give two branches for the resonance curve; in the case of coupled vibrations the two branches are separated by a silent zone; in the case of the solid rod they overlap, in qualitative agreement with the observations (1).

References

1. GIEBE, E. and BLECHSCHMIDT, E. Ann. Physik, 18 : 417-485. 1933.
2. POSENER, L. Ann. Physik, 22 : 101-128. 1935.
3. RÖHRICH, K. Z. Physik, 73 : 813-832. 1932.
4. RUEDY, R. Can. J. Research, 5 : 149-155. 1931.
5. SCHOENECK, H. Z. Physik, 92 : 390-406. 1935.

THE THERMAL CONDUCTIVITY OF SUNDRY MATERIALS¹

By C. D. NIVEN²

Abstract

The results of measurements on the thermal conductivity of acetylene black, rock wool, sphagnum moss, dried asbestos-water paste and other insulators are given.

The descriptions of the samples of insulating materials whose thermal conductivity is reported in this paper are those which the manufacturers furnished.

The results on sphagnum peat moss are of so much commercial interest at the present time that some results of Dr. Finck's (1), taken from a Bureau of Standards publication, are quoted in Table I. These results were obtained with dried material and are therefore slightly lower than those reported in Table II. The general agreement, however, is remarkably good.

TABLE I
THERMAL CONDUCTIVITY OF SPHAGNUM MOSS,
AS DETERMINED BY FINCK

Moisture,	Density, lb./cu.ft.	Mean temp., °F.	Conductivity, B.t.u./hr./ sq. ft./°F./in.
Negligible	3.0	90	0.251
Negligible	3.4	90	0.256
Negligible	4.5	90	0.248
Negligible	5.4	90	0.237
Negligible	9.9	90	0.278
Negligible	16.7	90	0.339

NOTE:—Quoted from Reference (1), p. 976.

be forgotten by those who would stress the economy which can be effected by its use.

The samples of rock wool, with one exception, were supplied by Mr. M. F. Goudge and are fully described by him in a memorandum (2) of the Mines Branch. The results indicate that the quality of the rock wool rather than the density of packing is the important factor affecting the thermal conductivity.

The samples of asbestos were prepared by Mr. D. Wolochow, chemist in charge of the asbestos research work undertaken by the Division of Chemistry of the National Research Council. The results of the experiments indicate that both the length of the fibre and the quantity of water used in making

There is an indication that the thermal conductivity of sphagnum peat moss increases linearly with the density and that the rate of increase is somewhat similar to that of wood fibre. This result is of course to be expected since compressing would mainly have the effect of squeezing the air out of the sample. Sphagnum peat moss is clearly a good insulator but its exceedingly hygroscopic nature should not

¹ Manuscript received April 18, 1935.
Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada.

² Physicist, National Research Laboratories, Ottawa.

TABLE II
DESCRIPTION AND THERMAL CONDUCTIVITY OF SAMPLES

Material	Description	Thickness at which sample was measured, in.	Moisture, %	Density, lb./cu. ft.	Mean temperature, °F.	Conductivity, B.t.u./hr./sq. ft./°F./in.
Acetylene black	50% compressed	1.117	0.7	5.5	53	0.268
	Uncompressed	1.090	1.5	2.2	55	0.220
Chopped straw	Treated for fire resistance	1.148	6.0	8.1	53	0.361
Corrugated board	Double, corrugations horizontal	0.335	—	11.8	53	0.366
Corrugated aircell insulating board	9/16 in., corrugations horizontal *	0.722	—	8.05	54	0.353
	5/16 in., corrugations horizontal	0.354	—	7.6	52	0.338
Rock wool	Long fibre, moderately coarse	1.083	Negligible	3.0	53	0.271
	Granulated	1.099	Negligible	8.7	53	0.280
	Fine, almost free from shot	1.100	Negligible	7.9	54	0.230
	Fine, containing considerable shot	1.110	Negligible	10.3	55	0.248
	Pad containing a small amount of bonding material	0.700	Negligible	11.3	54	0.248
		1.099	Negligible	7.9	55	0.242
		1.240	Negligible	6.6	55	0.242
	Commercial	1.100	Negligible	6.1	55	0.247
Specially ground wood fibres	Calcium treated	1.090	8	5.5	56	0.317
		1.190	7	6.0	57	0.328
Sphagnum peat moss	Board	1.328	11.0	10.2	59	0.309
	Loose	1.106	11.0	3.9	58	0.264
	Loose, charred	1.192	7.6	16.2	57	0.382
	Fine ground, moist	1.083	25	3.9	58	0.256
	Rough, very moist	1.114	30(?)	2.3	56	0.362
	Shredded	1.104	9.6	3.5	56	0.258
	Loose	1.183	10	8.5	59	0.271
		1.110	10	9.8	63	0.289
		1.102	10	4.7	59	0.272
Asbestos-water paste moulded by hand and dried*	Short fibre; 120% mixing water	0.698	Negligible	56	633	1.80
	Short fibre; 100% mixing water	0.731	Negligible	60	611	1.98
	Short fibre; 80% mixing water	0.826	Negligible	64	638	2.19
	Very short fibre; 100% mixing water	0.916	Negligible	64	608	2.39
	Very short fibre; 75% mixing water	0.808	Negligible	68	613	2.11
	Very short fibre; 65% mixing water	0.849	Negligible	74	643	1.99
	Fine ground serpentine; 80% mixing water	0.855	Negligible	69	634	1.69

* Short fibre refers to Quebec Standard Screen Test 0-0-4-12. Very short fibre refers to Quebec Standard Screen Test 0-0-1-15. The fine ground serpentine was 200 mesh material.

the samples affect the thermal conductivity. As shown in Table II, these measurements were carried out at a temperature much higher than the temperatures at which the other measurements were made, since, of course, asbestos is essentially an insulator for use at temperatures higher than room temperature.

References

1. FINCK, J. L. Bur. Standards J. Research, 5 : 973-984. 1930.
2. GOUDGE, M. F. Can. Dept. Mines, Mines Branch, Ottawa. Memorandum No. 62. 1934.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 13, SEC. B.

JULY, 1935

NUMBER 1

THE SORPTION OF WATER VAPOR ON CELLULOSIC MATERIALS¹

BY EDGAR FILBY² AND O. MAASS³

Abstract

A direct method used for measuring the adsorption of water vapor on cellulosic materials and in which a number of improvements have been made is described. It is ensured that no vapors other than water are present no matter how long a time is required for the establishment of equilibrium. The adsorption and desorption isotherms of standard cellulose, spruce wood, surgical cotton, Kodak rag cellulose and bleached sulphite have been measured, and the data which indicate the time required for the establishment of true equilibrium have been given. The data of Urquhart and Williams (6, 7) for standard cellulose determined by an indirect method in 1926 have been shown to be correct.

Introduction

This paper deals with the further development of a method used by one of us for measuring the sorption of vapors such as water and alcohol on adsorbing materials such as cellulose and wood.

A McBain-Bakr spring balance of quartz fibre, sensitive to about 1 part in 20,000 of the total weight suspended, is used to measure the sorption, which, at saturation, amounts to 20 or 30% of the dry weight.

The sample to be investigated is suspended on the spring balance in a glass tube and subjected to a constant vapor pressure by connecting the tube to a bulb containing the liquid sorbate. In this way the relative vapor pressure of the sample and that of the liquid used as the source of vapors may be regulated by thermostatically controlling each separately.

The system contained neither stopcocks nor mercury seals, since both are subject to criticism, the stopcocks developing leaks and the mercury being adsorbed appreciably on cellulose at high-vacuum pressures.

The curves as established are of the same "S"-form as that indicated by previous workers (1, 2, 4, 5, 6, 7); however the time required for equilibrium to be established is in some cases found to be considerably longer owing to the somewhat different technique employed.

¹ Manuscript received June 11, 1935.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada.

² Research Chemist, The Electric Reduction Company, Buckingham, Quebec.

³ Professor of Physical Chemistry, McGill University.

Apparatus

Experimental

As previously stated the McBain-Bakr (3) spring balance was made from a fine quartz fibre. These fibres were made by pulling out quartz rod after it had been heated in an oxy-acetylene flame, and were wound into spirals of half-inch diameter and about 50 turns to the inch by passing them through a small gas jet on to a revolving steel rod.

Each cell was constructed of glass tubing of about $2\frac{1}{2}$ ft. in length and one inch diameter. This was sealed off at both ends, with a hook at one end to which the balance and suspended sample could be attached. At a short distance from the hook end there was inserted a side tube that could be connected to the water bulb.

The two thermostats, one for the cells, the other for the water bulb, were fitted with cooling coils, heating lamps and thermoregulators, which were sensitive to 0.01° change in temperature. A diagram of the vacuum system is shown in Fig. 1 in which one cell and spring balance is drawn in full and the position of the other four indicated.

Manipulation

After the balances were made and fitted with central rods (W. B. Campbell (1)) as shown in Fig. 1, they were tested for Hook's law by measuring the length from the end of the central rod to the bottom of the spiral, shown in Fig. 2, with varying loads. The balance and sample were then suspended in the cell and the end sealed off, a process that required considerable technique.

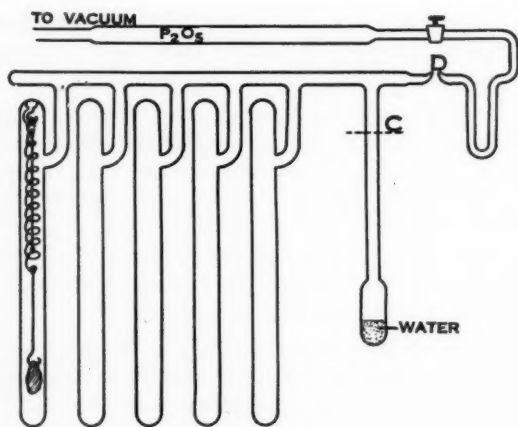


FIG. 1. Sorption measuring system.



FIG. 2. Quartz spiral.

When five cells, each containing a spring balance and suspended sample were fitted as shown in Fig. 1, the system was sealed at C, and evacuated through the phosphorus pentoxide tube which was surrounded by liquid air to

prevent contamination from the mercury vapor pumps at high-vacuum pressures. The entire system was flushed out several times with dry helium, then the pump left on for a few days until a pressure of less than 0.0001 mm. of mercury was registered in a McLeod gauge attached between the "U" tube and the pump. This low pressure was found to remain constant for 12 hr. after the pumps had been cut off.

During this process, measurements of the length shown between *A* and *B* Fig. 2, were read until the value was constant. The system was then filled with dry helium and the water bulb attached at *C*. The water in the bulb was freed from air by repeatedly freezing, cooling and evacuating it until such a procedure caused no change in pressure in the McLeod gauge. The system was again flushed out with helium, the water bulb was immersed in liquid air, and the process of evacuation allowed to continue until the pressure could not be read on the McLeod gauge. The system was then sealed off from the pumps and phosphorus pentoxide tube at *D*, leaving a closed evacuated system containing the sorption balance and solid and liquid phases to be studied.

The remainder of the experimental procedure consisted in measuring the length of the spiral balances under varying conditions of relative vapor pressures. This was done by keeping the cells at 20.0° C. and varying the temperature of the water bulb. First, the bulb was set at liquid air temperatures and left until equilibrium was established, readings on the spirals being taken every few hours. This was repeated at different temperatures each higher than the preceding one until finally the water bulb was thermostatically controlled at about 19° C., which gave a relative vapor pressure of about 94%. Water was then distilled from the bulb into the cells in order to saturate the samples. When this was accomplished the temperature of the water bulb was lowered and the vapor distilled off from the samples. Desorption equilibrium values were then obtained at various intervals until at liquid air temperatures the phosphorus pentoxide dry weight was again reached. In this manner the adsorption isotherm for the materials investigated were established. A calibrated Becker cathetometer was used to measure the length of the spirals.

Materials

A sample of white spruce wood 1 mm. thick was taken from the centre of a log. Cutting across the grain and limiting the thickness to 1 mm. was found to speed up diffusion of the vapor into the sample. The spruce wood was suspended on spiral balance No. 1.

Spiral balance No. 2 carried a piece of purified cotton obtained from bleached surgical cotton by seven 12-hr. extractions with 1% boiling sodium hydroxide, after which the cotton was washed free from base with distilled water. The process was completed by acidifying the cotton with 1% acetic acid and washing it free from acid.

The sample of standard cellulose on spiral balance No. 3 was prepared as follows. A 75 gm. batch of raw cotton that had been hand picked free from seeds and foreign matter was extracted with ethyl alcohol for four periods of four hours each. Four two-hour extractions were then carried out with diethyl ether, after which the cotton was subjected to a continuous ten hour extraction with 1% boiling sodium hydroxide, during which a total volume of 10 litres was used. The cotton was then washed with four litres of boiling water, and cold water, five to six litres, was added to cool the batch, which was then washed on a Buchner funnel with five litres of water and dried by means of a suction pump. The product was next soaked in 1% acetic acid for about two hours, washed free from acid with 10 litres of water and allowed to dry *in vacuo* at about 40° C. All solutions were made with distilled water, and all water used was previously boiled to expel dissolved oxygen.

Spiral balance No. 4 carried a sample of Kodak rag cellulose, and spiral balance No. 5, a sample of bleached sulphite pulp that had been allowed to stand in distilled water for a period of 12 hr.

Results

The spirals were carefully calibrated with known weights and tested for the relation $S = \frac{E}{W}$, where S is the sensitivity and E is the elongation caused by a weight of W grams. In the following tables are shown (i) the sorption values found when the samples were subjected to definite vapor pressures, and (ii) the desorption values of the same samples. In Table I the data recorded for standard cellulose are given in detail to indicate the time required for equilibrium to be established. Column 1 shows the time in hours, *i.e.* the time from the adjustment of the temperature of the water bulb to T_2° C. to the time of reading the length AB . T_1 is the temperature of the sample and T_2 that of the thermostat surrounding the water bulb. Where no temperature is recorded under T_2 it means that the sample was subjected to evacuation prior to the sealing off of the apparatus. L , in millimetres, is the distance between the points A and B , from which the elongation can be calculated. The first value at each temperature, T_2 , given is that at which equilibrium was expected, and the subsequent values are recorded to indicate further change if any. It will be seen that in the sorption at low vapor pressures, equilibrium is established fairly rapidly, but at higher pressures and for desorption long intervals of time are required. It is of interest to note that after desorption the liquid air value was the same within experimental error. The last two columns show the percentage of water and the percentage relative vapor pressure taken as the final value. The percentage of water sorbed by the sample was calculated in terms of the dry weight. The relative vapor pressure was calculated from data obtained from the International Critical Tables.

TABLE I

SORPTION OF WATER VAPOR ON STANDARD CELLULOSE AND DESORPTION OF WATER FROM STANDARD CELLULOSE SATURATED WITH WATER VAPOR

Time, hr.	T_1 , °C.	T_2 , °C.	L , mm.	E , mm.	% Water on sample	% R.v.p. in system
<i>Sorption</i>						
12	20.0		1.94			
36	20.0		1.90			
60	20.0		1.90			
84	20.0		1.94			
10	20.0	Liquid	1.95			
20	20.0	air	1.94			
17	20.0	Solid	1.96			
26	20.0	CO ₂ and	1.94			
40	20.0	ether	1.94			
1	20.0	-20	2.71			
3	20.0	-20	2.73	0.83	0.80	4.24
2	20.0	-6.5	4.89			
4	20.0	-6.5	4.87	2.98	2.85	15.11
24	20.0	0.0	5.77			
28	20.0	0.0	5.79			
36	20.0	0.0	5.79	3.89	3.73	26.12
32	20.0	11.5	8.85			
39	20.0	11.5	8.85			
46	20.0	11.5	8.86	6.96	6.66	58.04
13	20.0	12.0	9.21			
26	20.0	12.0	9.20			
31	20.0	12.0	9.20	7.30	6.98	59.98
20	20.0	14.0	10.27			
66	20.0	14.0	10.28			
78	20.0	14.0	10.27			
86	20.0	14.0	10.27	8.37	8.01	68.36
17	20.0	16.0	11.88			
54	20.0	16.0	11.84			
62	20.0	16.0	11.87			
86	20.0	16.0	11.88	9.98	9.56	77.75
23	20.0	19.0	17.69			
40	20.0	19.0	17.78			
80	20.0	19.0	17.77			
95	20.0	19.0	17.85	15.9	15.3	93.9
21	20.0	19.5	21.73			
42	20.0	19.5	21.79			
50	20.0	19.5	22.03			
65	20.0	19.5	21.60	20.	19.	96.9
10	20.0	20.1	100*			
58	20.0	20.1	54.0			
82	20.0	20.1	54.2			
94	20.0	20.1	55.0	53.	51	100

*The high saturation value found at the end of 10 hours was due to water condensing on the sides of the cell and being absorbed on the sample by actual contact.

TABLE I—*Concluded*SORPTION OF WATER VAPOR ON STANDARD CELLULOSE AND DESORPTION OF WATER FROM
STANDARD CELLULOSE SATURATED WITH WATER VAPOR

Time, hr.	T_1 , °C.	T_2 , °C.	L , mm.	E , mm.	% Water on sample	% R.v.p. in system
<i>Desorption</i>						
82	20.0	19.0	20.99			
115	20.0	19.0	21.06			
176	20.0	19.0	20.50			
194	20.0	19.0	20.45			
224	20.0	19.0	20.46	18.5	17.5	93.9
24	20.0	18.0	17.56			
94	20.0	18.0	17.34			
138	20.0	18.0	17.24			
160	20.0	18.0	17.25	15.3	14.5	88.3
24	20.0	16.0	14.37			
90	20.0	16.0	14.15			
128	20.0	16.0	14.09			
138	20.0	16.0	14.08	12.18	11.55	77.75
45	20.0	12.0	10.74			
60	20.0	12.0	10.69			
94	20.0	12.0	10.67			
108	20.0	12.0	10.67	8.77	8.30	59.98
12	20.0	8.0	9.10			
36	20.0	8.0	9.00			
60	20.0	8.0	9.00			
108	20.0	8.0	9.00	7.10	6.73	45.88
31	20.0	2.0	7.50			
48	20.0	2.0	7.45			
76	20.0	2.0	7.25			
110	20.0	2.0	7.25	5.35	5.07	30.2
6	20.0	-11.0	4.82			
24	20.0	-11.0	4.51			
48	20.0	-11.0	4.52			
60	20.0	-11.0	4.51	2.61	2.47	10.18
24	20.0	Solid	1.99			
48	20.0	CO ₂	1.95			
72	20.0	and	1.94			
96	20.0	ether	1.95			
12	20.0	Liquid	1.93			
25	20.0	air	1.90			
72	20.0		1.92			
95	20.0		1.91			

In Table II are recorded the final sorption and desorption values for the other samples.

In every case it was found that the weight *in vacuo* corresponded with the weight when the temperature was that of liquid air to within the accuracy with which measurements could be made.

TABLE II
SORPTION AND DESORPTION VALUES FOR VARIOUS CELLULOSIC MATERIALS

T_1 , °C.	T_2 , °C.	% Water in sample	% R.v.p. in system	T_1 , °C.	T_2 , °C.	% Water in system	% R.v.p. in system
Sorption				Desorption			
White spruce							
20.0	Liquid air			20.0	19.0	28.2	93.9
20.0	Solid CO ₂ and ether			20.0	18.0	24.1	88.3
20.0	-20	1.84	4.24	20.0	16.0	19.01	77.75
20.0	-6.5	4.60	15.11	20.0	12.0	14.13	59.98
20.0	0.0	6.23	26.12	20.0	8.0	11.37	45.88
20.0	11.5	11.53	58.04	20.0	2.0	8.41	30.20
20.0	12.0	11.96	59.98	20.0	-11.0	4.21	10.18
20.0	14.0	13.67	68.36	20.0	Solid CO ₂ and ether		
20.0	16.0	16.40	77.75		Liquid air		
20.0	19.0	25.2	93.9	20.0			
20.0	19.5	30	96.9				
20.0	20.1	35	100				
Bleached surgical cotton							
20.0	Liquid air			20.0	19.0	17.5	93.9
20.0	Solid CO ₂ and ether			20.0	18.0	14.3	88.3
20.0	-20.0	0.99	4.24	20.0	16.0	11.95	77.75
20.0	-6.5	2.82	15.11	20.0	12.0	7.92	59.98
20.0	0.0	3.64	26.12	20.0	8.0	6.23	45.88
20.0	11.5	6.44	38.04	20.0	2.0	4.64	30.20
20.0	12.0	6.74	29.88	20.0	-11.0	2.52	10.18
20.0	14.0	7.74	68.36	20.0	Solid CO ₂ and ether		
20.0	16.0	9.24	77.75	20.0	Liquid air		
20.0	19.0	15.2	93.9				
20.0	19.5	19	96.9				
20.0	20.1	32	100				
Kodak rag cellulose							
20.0	Liquid air			20.0	19.0	17.8	93.9
20.0	Solid CO ₂ and ether			20.0	18.0	14.5	88.3
20.0	-20	0.94	4.24	20.0	16.0	11.23	77.75
20.0	-6.5	2.60	15.11	20.0	12.0	7.97	59.98
20.0	0.0	3.46	26.12	20.0	8.0	6.26	45.88
20.0	11.5	6.49	58.04	20.0	2.0	4.64	30.20
20.0	12.0	6.77	59.98	20.0	-11.0	2.40	10.18
20.0	14.0	7.84	68.36	20.0	Solid CO ₂ and ether		
20.0	16.0	9.34	77.75	20.0	Liquid air		
20.0	19.0	15.4	93.9				
20.0	19.5	20	96.9				
20.0	20.1	39	100				

TABLE II—*Concluded*

SORPTION AND DESORPTION VALUES FOR VARIOUS CELLULOSIC MATERIALS

T_1 , °C.	T_2 , °C.	% Water in sample	% R.v.p. in system	T_1 , °C.	T_2 , °C.	% Water in system	% R.v.p. in system
Sorption				Desorption			
<i>Bleached sulphite pulp</i>							
20.0	Liquid air			20.0	19.0	21.3	93.9
20.0	Solid CO ₂			20.0	18.0	17.4	88.3
	and ether			20.0	16.0	13.30	77.75
20.0	—20	1.33	4.24	20.0	12.0	9.46	59.98
20.0	— 6.5	3.40	15.11	20.0	8.0	7.44	45.88
20.0	0.0	4.63	26.12	20.0	2.0	5.63	30.2
20.0	11.5	8.08	58.04	20.0	—11.0	3.94	10.18
20.0	12.0	8.48	59.98	20.0	Solid CO ₂		
20.0	14.0	9.67	68.36		and ether		
20.0	16.0	11.45	77.75	20.0	Liquid air		
20.0	19.0	19	93.9				
20.0	19.5	23	96.9				
20.0	20.1	33	100				

TABLE III

COMPARISON OF DATA OF AUTHORS WITH THAT OF URQUHART AND WILLIAMS

Relative humidity, %	Water in sample, %			
	Standard cellulose (F and M)	Bleached surgical cotton (F and M)	Kodak rag cellulose (F and M)	Scoured cotton (U and W)*
<i>Sorption</i>				
4.24	0.80	0.99	0.94	1.4
15.11	2.85	2.82	2.60	2.6
26.12	3.73	3.64	3.46	3.5
58.04	6.66	6.44	6.49	6.3
59.98	6.98	6.74	6.77	6.5
68.36	8.01	7.74	7.84	7.5
77.75	9.56	9.24	9.34	9.1
93.9	15.3	15.2	15.4	14.9
96.9	19.0	19.0	20.0	17.6
<i>Desorption</i>				
93.9	17.5	17.5	17.8	81.1
88.3	14.5	14.3	14.5	14.8
77.75	11.55	11.05	11.23	11.3
59.98	8.30	7.92	7.97	8.2
45.88	6.73	6.23	6.26	6.4
30.2	5.07	4.64	4.64	4.6
10.18	2.47	2.52	2.40	2.5

*Data received in private communication from A. R. Urquhart.

Discussion

A method for the determination of the sorption of water vapor on cellulosic materials has been described. The new features are greater sensitivity of spiral, elimination of all vapors including mercury and air, complete isolation of materials examined from contact with anything but water vapor over an indefinite period. To amplify the last statement it may be said that it is of advantage to subject the cellulosic materials to repeated hysteresis cycles in such a manner that the interference of such factors as contact with air, etc. is impossible. Finally when various cellulosic materials are to be compared the necessity of absolute identity of conditions for purposes of comparison is obvious.

The results obtained with cotton are found to be in agreement with those of Urquhart and Williams (Table III). In a paper by Maass and Pidgeon (4) the following statement was made regarding sorption measurements on wood and cotton:—

"Little of the work which has been done is entirely free from objection. In even the most careful determinations of the adsorption by cotton cellulose the amount of adsorption was measured indirectly." This statement is certainly erroneous in so far as the work of Urquhart and Williams is concerned. Their results are as nearly correct as it is possible to obtain them. On the contrary, the values obtained by Maass and Pidgeon at high relative humidities have been shown to be much too low, owing to inexperience regarding the time required for equilibrium to be established under these conditions. The main object of the paper of Maass and Pidgeon, to show the similarity in type of curve (sorption and desorption) between wood and cellulose and also to show the markedly greater adsorption by wood, has been amply confirmed both by Grace and Maass and the work described in this paper.

It may not be out of place to set forth the reasons why the direct method was considered to be the one giving more accurate values. It is probably true that in the indirect method the pressure is very rapidly equalized throughout a 100 cc. volume—so rapidly that sorption proceeds at uniform rate throughout the sample. This can be true, however, only in the entire absence of air or similar gas. Even a very small quantity of air will be driven by flow of water vapor into any pockets where sorption is taking place, and here sorption will be delayed by diffusion of vapor in one direction against diffusion of air in the opposite direction. In any case the main point is not whether sorption should take place at a constant vapor pressure, a phenomenon that is of course impossible, because it is necessary to cause a change in vapor pressure in order to cause sorption. The real point is whether the sample reaches its equilibrium by continual sorption *in one direction*, as compared with a part of the sample (whether that part be a part—the outside—of a single fibre or all the fibres) in one portion of the apparatus over-reaching the equilibrium value and then establishing equilibrium from the opposite direction. From the statement made by Urquhart and Williams (7) it is evident

that the vapor pressure is temporarily higher than the final value. Even assuming that the vapor pressure is equal throughout the space, this can mean only that outside layers of cellulose approach equilibrium with this high vapor pressure and later lose moisture, which is adsorbed by the inside layers. Hence the two portions reach the value from opposite directions. It is evident however that sorption is very rapid, since the cotton reduced the vapor pressure to 2 mm. although that of the water supply was 23.7 mm., but cooling, etc., delayed evaporation. Again, the tap was closed when the pressure was 11 mm. (63%), and the pressure sank to 8 mm. (46%). Some portion of the cotton must have almost reached equilibrium with the 63% relative vapor pressure, and later lost water to such an extent that equilibrium with 46% relative vapor pressure was established. The extent of this error depends on the size of the step taken and the portion of the curve concerned. If steps are small the error is small and this was undoubtedly the case in Urquhart and Williams' work.

Finally in regard to the foregoing it is left to the reader to judge the relative merits of the direct and indirect methods for measuring sorption on cellulosic materials. However, the data at high relative vapor pressures obtained by Maass and Pidgeon with cotton* are considerably too low, because time was not allowed for true equilibrium to be established, and their statement regarding the demerits of the indirect method is regretted. The errors, if any, supposed to be inherent in the indirect method, evidently had a negligible effect on the results of Urquhart and Williams.

References

1. CAMPBELL, W. B. Dept. of Interior, Canada. Bull. 84. 1933.
2. GRACE, N. H. and MAASS, O. J. Phys. Chem. 36 : 3046-3062. 1932.
3. MCBAIN, J. W. and BAKR, A. M. J. Am. Chem. Soc. 48 : 690-695. 1926.
4. PIDGEON, L. M. and MAASS, O. J. Am. Chem. Soc. 52 : 1053-1069. 1930.
5. SHEPPARD, S. E. and NEWSOME, P. T. Ind. Eng. Chem. 26 : 285-290. 1934.
6. URQUHART, A. R. and WILLIAMS, A. M. J. Textile Inst. 15 : T138-148. 1924.
7. URQUHART, A. R. and WILLIAMS, A. M. Shirley Inst. Mem. 3 : 49-307. 1924.

*Purification of the cotton sample used by Pidgeon and Maass was not as extensive as in the case of the samples examined in this investigation. Continued treatment with alkali (even 1%) increases the sorptive power of the cotton until a limiting value is reached. The isotherm obtained by Pidgeon and Maass is affine to that of Urquhart and Williams up to a relative humidity of 70%, the values being 17% lower in the former case. At relative humidities greater than 70% the values are too low as stated above, but differences due to the fact that equilibrium had not been established are not as large as would otherwise appear.

THE HYDROGENATION OF ALBERTA COALS

II. COMPARATIVE DATA ON THIRTEEN COALS OF VARIOUS RANKS AND TWO SUSPENSION MEDIA, TETRALIN AND LIQUID PETROLATUM¹

By E. H. BOOMER², A. W. SADDINGTON³, AND J. EDWARDS⁴

Abstract

Thirteen Alberta coals of graded rank have been hydrogenated in the presence of tetralin at 450° C. and in the presence of liquid petrolatum at 425° C. Tetralin is superior to liquid petrolatum owing, it is believed, to its efficiency as a hydrogen carrier and its solvent action on coal. The use of tetralin or materials of similar chemical constitution in a commercial process is considered possible, and the greater cost of the medium might be more than offset by its greater efficiency as compared with the ordinary heavy oils.

A definite progression from old to young coals has been shown by increasing yields of volatile oil, gas and water, and decreasing yields of pitch and coke.

Conversions of coal to oils, water and gas as high as 96.7% with tetralin and 81.6% with liquid petrolatum on the dry, ash-free basis have been reported.

Introduction

In the first paper of this series (4) the results of a preliminary investigation on the hydrogenation of three Alberta coals in various media were reported. This work gave evidence enabling a choice of favorable conditions for a more comprehensive investigation of Alberta coals.

The present paper deals with the hydrogenation of 13 coals of graded rank, including all classifications from semi-anthracite to lignite, by two standard methods. One series was carried out at 450° C. with tetralin (1,2,3,4-tetrahydronaphthalene) as suspension medium, and the other with liquid petrolatum as medium at 425° C. Molybdcic oxide was employed as catalyst in both series.

The results have confirmed the advantages of a medium such as tetralin, and thrown some further light on the mechanism of the reactions. They have shown that a hydrocarbon oil, typified by liquid petrolatum, can serve also, though less efficiently, as a suspension medium. Finally, the results demonstrate the suitability of several Alberta coals for use in the hydrogenation process in showing that lignitic coals, and to a lesser extent bituminous and sub-bituminous coals, can be converted nearly completely into liquid and gaseous products. The result would be important in the event that economic conditions warranted the use of the process as a source of oils. The primary economic requirements, both of which are fulfilled in Alberta, are sources of suitable cheap coal and hydrogen.

¹ Manuscript received March 20, 1935.

Contribution from the laboratories of the University of Alberta, Edmonton, Canada, with financial assistance from the National Research Council of Canada and the Research Council of Alberta.

² Associate Professor of Chemistry, University of Alberta.

³ Research Assistant, Research Council of Alberta, University of Alberta, 1929-1931. Present address: Solvay Corporation, Solvay, N.Y.

⁴ Research Assistant, Research Council of Alberta, University of Alberta, 1931-1933. Present address: McGill University, Montreal.

Materials and Apparatus

The series of 13 coals studied were obtained through the courtesy of Prof. E. Stansfield of the Research Council of Alberta. They were taken as samples in the ordinary course of the 1930 Alberta Coal Survey. A complete description and analysis of these coals is given in Tables I and II and in Fig. 1.

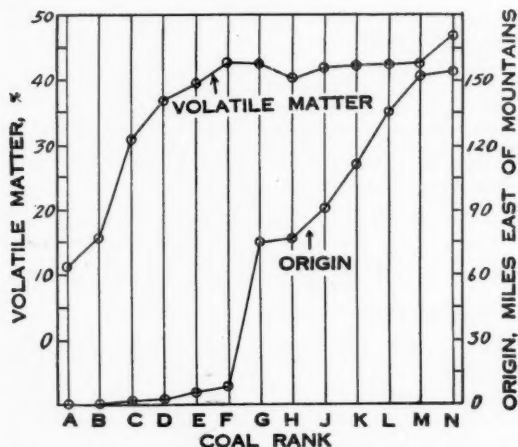


FIG. 1. Proximate analysis of dry, ash-free coal, and geographic origin of coals, in miles east of Rocky Mountains face.

properties through the sequence. First, there was an increase in moisture content; second and third, there was a decrease in calorific value and in carbon-hydrogen ratio, with decreasing maturity. Fig. 1 shows the proximate analysis of the coals in graphical form and the position of origin of each sample with respect to the eastern face of the Rocky Mountains. Samples A and B were taken on the mountain face, C and D in the foothills immediately east, E and F about 60 miles east of the mountain face; a more or less regular increase in distance from the mountain face will be noticed to N, a point 160 miles east. There is an obvious parallel between the rank of the coals and their geographical position. A similar parallel with regard to ease of hydrogenation has been found.

The samples, stored under water when received, were filtered, ground to somewhat less than pea size, and dried in a current of Viking natural gas at 110° C. and at a pressure of 25 mm. of mercury. This gas, mostly methane, was dry and free from sulphur. Immediately after drying, the coal was transferred to a ball mill in which it was ground to pass a 100 mesh sieve. The coal was used within 24 hr. of its preparation.

Commercial electrolytic hydrogen, stored in steel cylinders, was used. The catalyst was in every case molybdc oxide prepared by the dehydration of molybdc acid just below dull red heat.

The authors wish to acknowledge gratefully the assistance and advice in regard to the analytical data so generously provided by Professor Stansfield and Mr. W. A. Lang of the same laboratory.

The coals have been arranged in order of maturity, and have been assigned letters in order of the sequence, in addition to their sample number. The sequence starts with A, a semi-anthracite coal and ends with N, a lignite coal. The coals showed definite trends in three general

TABLE I
COALS OF 1930 ALBERTA SURVEY

Coal	Geological horizon	Canadian classification	Analysis of pure dry coal, S, etc., omitted			Seyler's classification	Calorific value, B.t.u./lb. pure, moist coal	Ulmins soluble in potash, % of pure dry coal	Fuel ratio FC/VM as received
			C	H	O + N				
A	Kootenay	Semi-anthracite	93.05	4.05	2.90	Ortho-carbonaceous	15,380	0.05	7.5
B	Kootenay	Semi-bituminous	91.40	4.40	4.20	Ortho-carbonaceous	15,560	0.0	5.4
C	Kootenay	Bituminous	88.7	5.20	6.10	Ortho-bituminous	15,380	0.0	2.25
D	Kootenay	Bituminous	87.65	5.60	6.75	Ortho-bituminous	15,490	0.02	1.75
E	Kootenay	Bituminous	85.10	5.55	9.35	Para-bituminous	14,610	0.16	1.70
F	Belly River	Sub-bituminous	83.80	6.05	10.15	Meta-per-lignitous	14,240	1.9	1.19
G	Belly River	Domestic	79.5	5.4	15.1	Ortho-lignitous	12,580	11.5	1.35
H	Edmonton	Domestic	78.95	5.30	15.75	Ortho-lignitous	11,880	47.1	1.32
J	Belly River	Domestic	77.9	5.2	16.9	Ortho-lignitous	11,320	13.6	1.40
K	Belly River	Domestic	77.40	5.15	17.45	Ortho-lignitous	10,370	39.5	1.36
L	Belly River	Domestic	75.40	5.25	19.35	Ortho-lignitous	9,940	49.7	1.50
M	Belly River	Domestic	73.5	5.2	21.3	Lignite	9,250	54.1	1.45
N	Edmonton or younger	Domestic	71.95	5.15	22.9	Lignite	8,420	60.2	1.12

NOTE:—FC/VM = ratio of fixed carbon to volatile matter.

TABLE II
COALS OF ALBERTA 1930 SURVEY

Sample	Location	H ₂ O, as received	Ultimate analysis, dry basis						
			C	H	Ash	S	N	O	C/H
A, 306/30	Anthracite	2.2	80.50	3.50	12.0	1.00	1.1	1.9	23.0
			92.45	4.00	—	0.65	1.3	1.6	23.1
B, 307/30	Canmore	1.4	85.10	4.05	6.0	0.75	1.5	2.6	21.0
			90.65	4.35	—	0.80	1.7	2.5	20.8
C, 303/30	Coleman	1.4	81.35	4.70	7.3	0.45	1.2	5.0	17.3
			88.30	5.15	—	0.45	1.3	4.8	17.1
D, 302/30	Bellevue	1.2	73.45	5.55	15.1	0.60	1.3	5.0	16.1
			87.25	5.60	—	0.45	1.5	5.2	15.6
E, 305/30	Pincher Creek	3.3	76.10	4.75	10.1	1.15	0.7	7.2	16.0
			84.70	5.55	—	0.45	1.2	8.1	15.3
F, 304/30	Lundbreck	4.9	70.55	5.00	13.9	0.85	1.9	7.8	14.1
			83.30	6.00	—	0.60	2.3	7.8	13.9
G, 301/30	Lethbridge	9.8	70.15	4.80	10.8	0.75	1.8	11.7	14.6
			79.10	5.35	—	0.55	1.9	13.1	14.8
H, 308/30	Champion	12.9	70.90	4.80	7.7	0.40	1.3	14.9	14.8
			78.65	5.30	—	0.35	1.3	14.4	14.8
J, 309/30	Taber	15.0	69.95	4.75	8.8	1.10	1.7	13.7	14.7
			77.40	5.15	—	0.65	2.0	14.8	15.0
K, 310/30	Grassy Lake	18.8	67.85	4.65	10.6	1.20	1.4	14.3	14.6
			76.70	5.10	—	0.90	1.9	15.4	15.0
L, 311/30	Winnifred	22.6	68.30	4.40	10.0	0.60	1.3	15.4	15.5
			74.90	5.20	—	0.70	1.4	17.8	14.4
M, 313/30	Redcliff	26.6	67.65	4.35	10.4	0.50	0.8	16.3	15.6
			73.10	5.15	—	0.55	1.1	20.1	14.2
N, 312/30	Eagle Butte	30.3	60.70	3.95	12.2	0.35	1.2	21.6	15.4
			71.65	5.15	—	0.40	1.1	21.7	13.9

NOTE:—Ultimate analysis—dry basis in first line—dry, ash-free basis, taken from curves, in second line—for each coal.

Two suspension media were used, tetralin and a paraffin oil fraction of medicinal grade known as liquid petrolatum, B.P. The tetralin was the 1,2,3,4- isomer and of the grade supplied by Eastman (b.p. 202–204° C.). The results of the A.S.T.M. distillation of the liquid petrolatum are given in Table III.

The apparatus, consisting of the storage system, autoclave, and auxiliary

TABLE III
A.S.T.M. DISTILLATION OF LIQUID PETROLATUM

Initial boiling point 152° C.	
10% over at 327° C.	70% over at 380° C.
20% over at 345° C.	80% over at 385° C.
30% over at 357° C.	90% over at 395° C.
40% over at 365° C.	
50% over at 371° C.	3½% over at 300° C.
60% over at 376° C.	91½% over at 400° C.

equipment, has been described in detail (3). Pressure measurements were made with a Bourdon tube gauge calibrated at intervals with a standard test gauge. Temperature measurements, made with a calibrated iron-constantan thermocouple, were indicated on a recording potentiometer controller. The instrument permitted control to within $\pm 5^\circ \text{C}$.

Gas analyses were made with an improved type of Bureau of Mines apparatus.

Experimental Procedure

Approximately 200-gm. samples of the dry powdered coal were mixed with the desired quantity of suspension medium and 5% by weight of molybdc oxide was thoroughly incorporated with the mixture. One hundred and fifty grams of tetralin was found to produce a sufficiently fluid charge, but 200 gm. of liquid petrolatum was required. The resulting paste was transferred to the autoclave, the weight added being accurately determined, the apparatus sealed gas-tight and, after washing out the air with natural gas, hydrogen added to give the desired initial pressure. Oscillation was started when the autoclave reached a temperature of about 100°C . The reaction mixture reached 425°C . in $2\frac{1}{2}$ to $2\frac{3}{4}$ hr., and 450°C . in $2\frac{3}{4}$ to 3 hr. The reaction chamber was maintained at the desired operating temperature for a period of four hours, during which a steady decrease in pressure indicated a corresponding absorption of hydrogen. No attempt was made to counteract the possible catalytic effect of the steel walls of the autoclave.

At the end of the four hour interval, heating was stopped and the autoclave allowed to cool overnight. The residual gases were bled through the expansion valve the following morning and led through activated charcoal absorbers, after which they were measured in an oil-filled wet-test meter before storage in a water-sealed gas holder. The gas was allowed to stand until it was of uniform composition, and a sample was drawn off for analysis. The increase in weight of the charcoal absorbers was noted and the spent absorbent revived by steam distillation. The yield of condensable products was noted and the gas volume measured in most instances.

The autoclave was recharged with hydrogen and a second cycle completed in a manner identical with that described above. The reaction chamber was then opened and the contents withdrawn as rapidly as possible, weighed and transferred to a glass-stoppered vessel. In spite of the precautions taken the volatile nature of some of the constituents of this mixture resulted in high evaporative losses. The reported oil yield is consequently low in all experiments. In the experiments in which liquid petrolatum was used, a hard brittle coke adhering to the walls of the autoclave and which was removed with difficulty was often encountered. The estimated loss of solid products in such cases was 10 gm.

The yield of solid and liquid products was estimated in the following manner. The oily mass from the autoclave was filtered by suction and the residual solids washed with ether and subsequently dried and weighed. The

weight of dried coke less the weight of catalyst used thus represented the solid residue from the coal, together with any coke formed in the decomposition of the charge. In this way the oil yield was determined as the difference between the total weight of reaction products extracted from the autoclave and the dried solid residue.

The filtrate from the ether washing was distilled to recover the ether, the distillation residue being added to the oil obtained by filtration. The combined oils were then subjected to distillation analysis. The first fraction, that boiling below 175° C., usually contained a large amount of water. The yields of oil and water were recorded separately. The second and largest fraction was that distilling between 175 and 225° C., and, in the experiments in which tetralin was used, included all the tetralin as well as any decalin or naphthalene formed. The final fraction, taken up to 300° C., was small and included a reddish, viscous oil of evident lubricating value. On occasion wax-like crystals were obtained at about 280° C. The residue from the distillation was a stable pitch boiling at temperatures as high as 450° C. without decomposition. The consistency of the pitch depended upon the coal and the medium used. The pitch was of particular interest in that it closely resembled the residues obtained from distillation analyses of the products of hydrogenation of bitumen from the McMurray bituminous sand deposits (3). The distillation data of oils obtained in the experiments using liquid petrolatum when plotted gave a smooth curve showing no evidence of particular fractions. The water content was lower and the yield of pitch was considerably higher than they were when tetralin was used. The pitch was much softer than that obtained in the tetralin series.

The yield of gaseous products and the hydrogen absorption were calculated from gas analyses and total gas volume data. In estimating the amount of hydrogen absorbed, two procedures were used. In the petrolatum series it was assumed that both the medium and the coal were reduced, but in the tetralin series the absorption of the hydrogen was attributed to the coal alone.

It is uncertain how much hydrogen was absorbed by the medium, but it is probable that it was considerably less with tetralin than in the experiments with petrolatum. Lush (10) has shown that tetralin is the final product of the hydrogenation of naphthalene at much lower temperatures, and Hall (5) has found that little production of low boiling material occurs under comparable conditions up to 400° C. However, Hall found considerable production of low boiling material but little of decalin or naphthalene when tetralin was hydrogenated at 450° C. Hall gives data on hydrogen absorption for naphthalene only, but on the basis of his tabulated pressure changes and gas compositions in comparable experiments with naphthalene and tetralin, the absorption with tetralin is less than one-half that with naphthalene. Comparing with the experiments reported here, a maximum absorption by the medium of 2.5% by weight may occur. Under the more complex conditions obtaining when coal is a competitor for a limited supply of hydrogen, a much smaller absorption of hydrogen by the medium may be expected.

Results and Discussion

Hydrogenation in the Presence of Tetralin

The results obtained in the hydrogenation of the 13 coals are presented in Table IV. For the most part the data will need no interpretation but it will be well to define precisely some of the expressions used.

The amount of hydrogen absorbed is given as percentage by weight of the coal put into the autoclave. The gas yield in litres per kilogram of charge is calculated on the same basis, and is derived from the volume of gas, less hydrogen, removed from the autoclave. The percentages converted to gases, liquids and solid residue are based on the total charge, including the catalyst, and for this reason the figures given for the solid residue recovered include the catalyst. The percentage loss is thus the difference between 100 and the sum of the percentages of the recovered products. The values for the gas analysis are averages of those for each cycle, account being taken of the gas volumes in each case. The figures on total conversions are obtained by subtracting the weight of the solid residue removed from the autoclave, not including catalyst, from the dry coal charged. They thus represent the percentage of the coal converted to oil, gas and water. To calculate the conversion of the coal on the basis of dry, ash-free coal it is necessary only to divide these figures by the difference between one and the fraction of the dry coal that is ash. Conversions on the basis of dry, ash-free coal are consequently higher.

The distillation analyses have been included in order to show the percentage conversion of the total charge to oils in the respective boiling ranges cited. The loss shown at the end of this section represents the distillation losses only. The total oil and water distillate to 300° C. plus the yield of residual pitch, plus the distillation loss, adds up to the total conversion of the charge to liquid products.

The results in Table IV indicate clearly the definite progression in susceptibility to hydrogenation from old to young coals. Numerous small discrepancies will be noted but for the most part these are within the experimental error. The hydrogen absorption increases roughly from 3.9 to 4.4% for anthracite coals to an average value of 6.0% for domestic coals. In this respect Experiment 165 on Coal L-311 represents an interesting departure from the normal. It will be noted that the initial pressure of hydrogen was low. Hence it may be suggested that the extent of reaction depends on the concentration of hydrogen to some extent.

The discrepancy in Experiment 161 on Coal J-309 is not large and probably within experimental error. The remaining experiments fall into a fairly normal progression from the point of view of hydrogen absorption.

In agreement with this tendency to increased hydrogen absorption, an inspection of the pressure-time relations indicates that the rate as well as the amount of hydrogen absorption also increases as the age of the coal decreases. In Fig. 2, the pressure-time relations are given for the first cycles of experiments conducted with representative coals of various rank. The temperature reached 450° C. in about three hours or less. The rate of

TABLE IV
HYDROGENATION OF ALBERTA COALS IN THE PRESENCE OF TETRALIN

Experiment number	146	148	151	171	155	144	157	159	161	163	165	167	169
Sample number	A-306	B-307	C-303	D-302	E-305	F-304	G-301	H-308	J-309	K-310	L-311	M-313	N-312
Weight of coal, gm.	186	195	185	194	191	200	204	200	189	193	194	195	199
Weight of tetralin, gm.	144	146	138	146	144	132	149	148	144	145	146	151	147
Average initial pressure, lb./sq. in.	960	940	995	1015	1000	920	1000	990	1045	1000	790	970	1030
Average maximum pressure, lb./sq. in.	2545	2500	2595	2620	2570	2525	2665	2855	2950	2785	2570	2715	3195
Average final pressure, lb./sq. in.	660	595	525	530	510	450	475	505	585	485	410	510	545
Average pressure drop, lb./sq. in.	300	345	470	385	490	470	525	485	460	515	380	460	485
Hydrogen absorbed, %	3.9	4.4	6.0	5.7	5.3	5.5	5.8	5.6	5.5	6.2	4.5	5.6	5.9
Gas yield, less H ₂ , L/kg. of charge	76.8	74.8	110.8	98.8	75.7	117.0	100.0	111.0	85.3	113.8	96.0	105.6	119.0
Charge to liquids, %	35.5	46.8	69.0	69.5	67.7	60.2	65.5	61.2	65.4	66.0	64.5	65.0	64.3
Charge to solid residue, %	52.4	41.3	23.5	18.6	16.9	15.7	14.7	14.4	11.5	11.6	13.2	10.8	10.8
Charge to gas (including gas from charcoal), %	6.0	6.7	8.5	8.4	7.8	9.9	9.4	11.2	12.3	11.0	9.6	10.2	10.8
Charge to loss, %	6.1	5.2	0.0	3.5	7.6	14.2	10.4	13.2	10.8	11.4	12.3	14.0	14.1
Gas analysis, %													
CO ₂	0.2	0.2	2.2	1.0	0.4	1.3	2.9	4.4	3.9	4.2	7.3	7.2	8.8
C ₂ H ₆	0.4	0.4	0.4	0.5	0.5	0.6	0.7	0.2	0.1	0.1	0.3	0.1	0.3
H ₂	77.3	74.5	60.9	63.4	72.0	52.4	56.5	57.5	71.5	54.5	56.2	57.5	56.6
CO	0.6	0.6	1.7	0.7	1.0	1.4	1.9	1.1	1.2	3.2	1.6	2.0	2.1
C ₂ H ₄	4.5	5.5	8.7	9.7	7.2	13.1	14.7	12.0	9.0	24.8	10.8	10.9	11.3
CH ₄	9.9	12.1	16.0	12.7	11.0	25.2	14.3	27.7	25.8	16.1	19.0	21.0	20.2
Coal converted (dry coal), %	10.8	32.3	64.6	73.5	77.0	80.0	80.5	86.3	86.4	86.3	83.0	87.7	88.0
Coal converted (dry, ash-free coal), %	12.2	34.9	72.3	85.0	87.0	92.0	90.7	89.3	95.1	95.7	91.2	96.7	96.2
Charge to volatile products absorbed in charcoal, %	2.3	2.8	3.0	3.4	3.7	2.6	3.3	3.3	3.8	3.7	3.7	3.3	3.1
Charge to oil, %—(1) Oil to 175° C.	3.6	3.6	5.4	6.1	3.6	10.8	7.3	6.8	6.7	7.9	7.2	7.1	7.4
(2) Oil to 225° C.	27.7	30.4	41.9	43.1	37.6	37.9	34.7	36.0	39.1	36.7	36.6	37.5	37.0
(3) Oil to 300° C.	30.0	32.3	45.0	49.5	45.4	44.5	43.2	42.7	46.6	46.5	43.8	46.5	44.8
(4) Pitch	5.5	14.5	23.7	19.4	20.7	14.2	15.9	13.2	14.6	10.6	12.0	12.3	9.6
(5) Water	0.0	0.0	0.3	Trace	1.3	0.6	6.3	5.0	4.2	7.9	8.7	5.6	8.7
(6) Loss	0.0	0.0	0.0	0.6	0.3	0.9	0.0	0.3	0.0	0.0	0.0	0.6	1.2

reaction some time after hydrogenation has begun is indicated by the downward slope of the curve, and the total drop in pressure is a rough measure of the amount of hydrogen absorbed. Thus, for an anthracite coal the rate

of reaction is low and the total absorption is small. For bituminous and sub-bituminous coals the rate of reaction appears to be much the same, but the younger coal exhibits a much greater absorption. The extremely rapid absorption of hydrogen by domestic coals is clearly illustrated in the fourth curve.

A similar analysis was made of the pressure-temperature relations in these four experiments and it was noted that the temperature at which hydrogenation begins, as shown by changing curvature and heat evolution, decreased regularly from about 400° C. for semi-anthracite to less than 300° for domestic coal. Layng (9) has pointed out that a decrease in the temperature of plasticity of coals becomes apparent when the

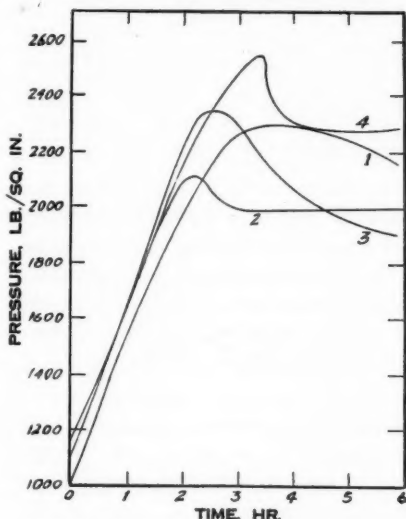


FIG. 2. Pressure-time relations, first cycle, tetralin medium. 1—Semi-anthracite, A; 2—bituminous, C; 3—sub-bituminous, G; 4—domestic, J.

coals are arranged in descending order of maturity. The exact relation of temperature of plasticity and the initial stages of hydrogenation has received the attention of Arend (1).

Fig. 3 presents the pressure-time relations of the second cycle of experiments on the same four coals with which the results shown in Fig. 2 were obtained. It will be noted that a higher temperature is required for hydrogenation to take place when a coal has previously been attacked by hydrogen. Apparently the less stable constituents become hydrogenated in the first cycle. It is further evident from these curves that the residues after the first cycle are more nearly alike than were the

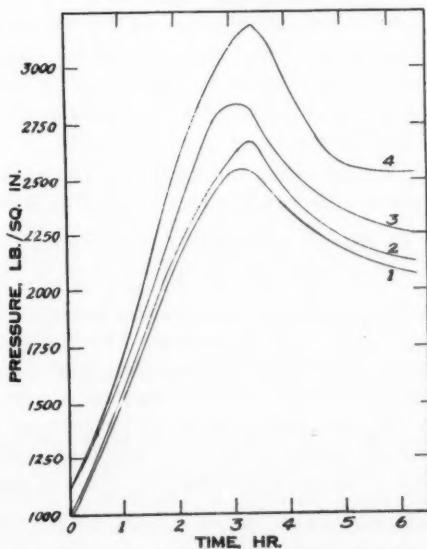


FIG. 3. Pressure-time relations, second cycle, tetralin medium. Coals as in Fig. 2.

original coals. This evidence is of importance in the application of hydrogenation to a continuous process. It appears that under the conditions most suitable for partial hydrogenation of fresh material the reaction is not complete, and more drastic conditions are necessary to obtain further reduction. The use of a higher temperature in the first cycle would lead to the formation of excessive amounts of gas and coke. Thus the evidence shows that satisfactory results, with particular regard to speed of reaction, would be obtained in continuous operation if apparatus designed for successive treatments at higher temperatures were used.

A further inspection of Table IV shows a definite increase in gas production as the coals decrease in age. Coincident with this is the tendency toward the development of higher maximum pressures. Analysis of the exit gases shows a pronounced increase in the carbon dioxide and carbon monoxide yields. The extent to which the coals became oxidized during milling and storing is difficult to estimate. The susceptibility to oxidation that is characteristic of young coals may account, in some measure, for the increased production of oxygenated compounds.

Paralleling this tendency to increased yields of carbon monoxide and carbon dioxide, the formation of water takes place to a greater extent with younger coals. It is probable that water is formed by reduction and decomposition of oxygen-containing groups such as hydroxyl in the coal. This subject will be more fully discussed later.

From Table IV it is further apparent that there is a general tendency toward increased mechanical losses with decrease in age of the coals. This may be taken as indicating an increasing conversion to low-boiling oils. Appreciable amounts of propane, butane and other volatile hydrocarbons appeared in the charcoal absorbers, and this, with the excessive amounts of carbon dioxide formed in the combustion analyses of the residual gases, further supports this view.

Though numerous small discrepancies are apparent there is a tendency toward a decrease in residual hydrogen with decreasing maturity of the coals.

In general the relative conversions to light oil, gas and water increase at the expense of the pitch formation, with decreasing maturity of the coals.

Two experiments on domestic coals (Experiments 165 on L-311 and 167 on M-313) were characterized by the appearance of considerable naphthalene in the reaction products. This would suggest that the reaction was incomplete after eight hours of operation. As has been previously mentioned, the initial hydrogen pressure in Experiment 165 was quite low. The formation of naphthalene in spite of the appreciable quantity of hydrogen present indicates the effective reducing action of tetralin.

Fractionation of the 175-225° C. fraction was carried out in a few cases with the lower-rank coals. Between 192 and 215° C. at 700 mm. pressure there was a halt in the temperature-volume curve while 60% to 70% of the

fraction came over, the last portions being naphthalene. Assuming this material to be tetralin, decalin and naphthalene, the recovery of medium was between 40 and 50% of the initial quantity used. The loss may be assigned to the decomposition of tetralin into low-boiling products.

A study of the data from the point of view of oil yield alone suggests that low grade bituminous or sub-bituminous coals are the most suitable for the process. The ease of hydrogenation and lower cost of domestic coals may be so favorable, however, as to make them the more suitable coals in spite of the higher water and gas production. The evidence is not conclusive.

Hydrogenation in the Presence of Liquid Petrolatum

Though the behavior of the coals upon hydrogenation in a liquid petrolatum medium was in general the same as that in tetralin, the conversions and general efficiency of the process were definitely poorer.

The results of this series of experiments are shown in Table V. The lines have the same significance as in Table IV, excepting "Hydrogen absorbed". It will be noted, however, that larger amounts of suspension medium were used, and that the hydrogen absorption was lower than that with the tetralin. This is due in part to the method of calculation, in which the whole charge was considered. Furthermore, these experiments were made at 425° C. as compared with 450° with tetralin. The reason for this lies in the greater stability of tetralin to heat. Extensive decomposition of liquid petrolatum takes place at 450° C. with the formation of gas and coke. It was not possible to determine what part of the gas and solid residue production in these experiments could be attributed to the medium.

An inspection of the table shows the expected increase in gas production and in maximum reaction pressures with decrease in maturity of the coal. The exception in Experiment 152 on Coal C-303 cannot be explained on the grounds of technique. The exit gas was unusually low in hydrogen. The excessive gas yields in Experiments 164 with Coal K-310 and 166 with Coal L-311 may be attributed to a higher temperature of operation. The former experiment got out of control and the temperature rose to 440° C. for a short time. Experiment 166 was also out of control and the temperature rose momentarily to 470° C. and was greater than 430° for 45 min. The excessive coke yield and low conversion to liquids that occurred in this experiment may also be attributed to the high operating temperature. More reliable data regarding the coal may be obtained from Experiments 163 and 165 of the tetralin series.

From Table V the same conclusions regarding high evaporation losses and high conversion to low-boiling oils and water may be drawn as in the tetralin series. It will be noted that in general the formation of water in this series of experiments is decidedly lower than that in the tetralin series, but the carbon dioxide formation is much the same.

TABLE V
HYDROGENATION OF ALBERTA COALS IN THE PRESENCE OF LIQUID PETROLATUM

Experiment number	147	149	152	154	156	145	158	160	162	164	166	168	170
Sample number	A-306	B-307	C-303	D-302	E-305	F-304	G-301	H-308	J-309	K-310	L-311	M-313	N-312
Weight of coal, gm.	197	194	191	195	190	179	193	194	188	189	195	193	196
Weight of solvent, gm.	197	204	191	205	201	179	195	200	195	189	195	193	199
Average initial pressure, lb./sq. in.	920	880	990	1030	1015	985	970	985	1015	1005	970	995	970
Average maximum pressure, lb./sq. in.	2195	2080	2380	2405	2480	2525	2500	2480	2645	2670	3050	2740	2950
Average final pressure, lb./sq. in.	725	660	570	645	610	570	510	605	555	565	610	565	575
Average pressure drop, lb./sq. in.	195	220	420	385	405	415	460	380	460	440	360	430	395
Hydrogen absorbed, %	1.0	1.4	2.6	2.1	2.2	2.5	2.5	2.5	2.6	2.6	2.4	2.5	2.4
Gas yield, less H ₂ in l./kg. of charge	37.5	40.4	116.2	45.2	65.0	71.5	79.5	82.5	66.0	92.5	137.0	78.3	87.0
Charge to liquids, %	38.5	44.6	49.5	54.0	57.2	59.6	53.2	56.8	57.8	59.8	41.3	56.7	64.3
Charge to solid residue, %	48.5	46.8	33.0	33.7	28.8	28.5	25.8	23.0	22.8	22.4	30.0	25.1	16.7
Charge to gas and charcoal, %	5.4	5.7	9.1	4.9	7.6	7.8	8.8	10.1	7.3	10.2	16.0	8.6	9.0
Charge as loss, %	7.6	2.9	8.4	7.4	6.4	4.1	12.2	10.1	12.1	7.6	12.7	9.6	10.0
Gas analysis, %													
CO ₂	0.2	0.3	6.3	0.3	0.4	0.6	2.7	4.3	3.6	4.8	7.6	6.5	9.0
C ₂ H ₆	0.3	0.3	0.2	0.4	0.3	0.5	0.5	0.5	0.1	0.2	nil	0.3	0.2
H ₂	87.0	83.5	52.8	81.5	74.8	73.7	65.4	63.5	71.8	62.5	53.7	67.6	62.8
CO	0.4	0.2	2.9	0.4	1.4	1.3	1.0	1.6	1.2	3.0	2.7	2.3	2.0
C ₂ H ₄	3.8	1.6	6.7	3.3	3.7	6.8	11.3	13.7	7.8	12.1	27.8	9.3	10.4
CH ₄	2.4	8.7	15.7	7.3	12.0	11.9	10.0	13.2	14.4	18.8	11.5	10.8	13.5
Coal converted (dry coal), %	7.1	9.3	40.8	37.7	47.9	50.3	55.6	61.0	61.8	63.0	46.9	57.5	74.6
Coal converted (dry, ash-free basis), %	8.0	10.1	45.6	43.6	54.2	57.7	62.6	66.9	68.1	69.9	51.4	63.4	81.6
Charge to volatile products absorbed in charcoal, %	3.7	3.8	4.0	2.9	4.6	3.2	4.2	4.4	3.0	4.3	3.7	3.7	3.4
Charge to oil, %—(1) Oil to 175° C.	6.6	7.8	12.8	9.1	8.2	11.7	9.9	13.0	9.4	12.6	11.8	9.4	10.7
(2) Oil to 225° C.	12.6	12.0	21.0	15.0	15.9	20.7	19.2	22.5	17.0	22.1	19.2	16.3	17.5
(3) Oil to 300° C.	20.2	20.1	32.7	25.4	26.7	34.0	29.3	33.0	28.7	32.5	26.9	29.3	30.5
(4) Pitch	18.3	23.9	15.4	28.6	28.1	23.4	20.0	20.0	25.2	22.4	9.1	23.8	24.6
(5) Water	0.0	0.0	1.4	0.0	1.9	2.2	3.9	3.5	3.6	4.6	5.0	3.3	7.1
(6) Loss	0.0	0.6	0.0	0.0	0.5	0.0	0.0	0.3	0.3	0.3	0.3	0.3	2.0

Figs. 4 and 5 represent the pressure-time relations of the first and second cycles of experiments conducted with four typical coals, three of which correspond to those with which the results shown in Figs. 2 and 3 were obtained. It will be seen that again hydrogen absorption is greatest and most rapid with domestic coals. Sub-bituminous and bituminous coals exhibit appreciable absorption, though the reaction rate is lower than that of domestic coals, and the slight effect of hydrogen on anthracite coal is again brought out.

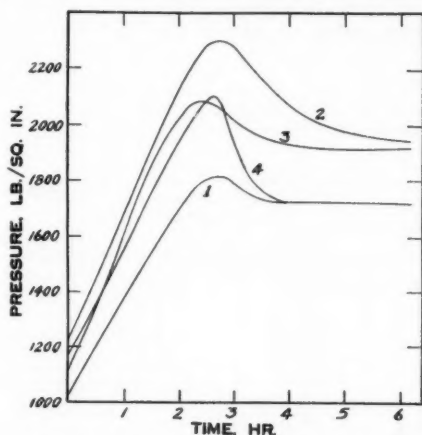


FIG. 4. Pressure-time relations, first cycle, liquid petrolatum medium. 1—Semi-anthracite, A; 2—bituminous, C; 3—sub-bituminous, G; 4—domestic, H.

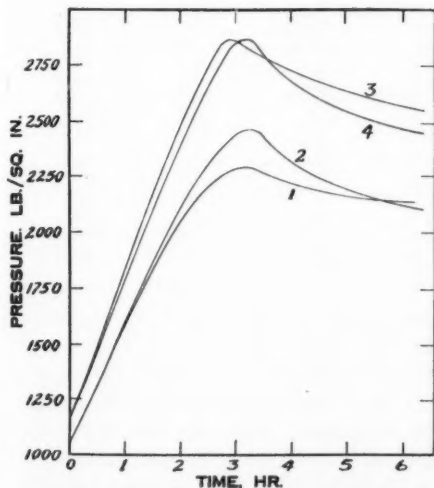


FIG. 5. Pressure-time relations, second cycle, liquid petrolatum medium. Coals as in Fig. 4.

Yields of oil, gas and water as high as 75% from a domestic coal under the conditions employed indicate that heavy petroleum oils such as liquid petrolatum might be suitable vehicles in which to suspend the coal. It is to be expected that conditions, differing for each coal, could be found such that higher conversions would take place, but the procedure in this investigation was standardized so as to form a basis for comparison of the coals studied.

As was the case with the tetralin series, the evidence of these experiments suggests bituminous or lower grade coals as most suitable for the process. A definite choice requires a study of costs, and additional experiments for the purpose of ascertaining optimum conditions for each grade of coal.

Comparison of Tetralin and Liquid Petrolatum as Suspension Media

The definite superiority of tetralin as a suspension medium for coal is shown by higher hydrogen absorption and lower coke formation than occurs in the petrolatum series.

Carbon dioxide production is much the same with both solvents, indicating no special tendency of tetralin to aid in the decomposition of carboxyl groups in the coal. Water formation is definitely

greater in the tetralin series and indicates reduction of oxygenated compounds which are not reduced by hydrogen with a liquid petrolatum medium.

The formation of ammonia in certain experiments in which tetralin was used indicated the reduction of nitrogenous material, whereas the absence of ammonia as a product of reaction in any of the experiments of the petrolatum series showed that a milder reduction had taken place. Ammonia formation in the tetralin may be due, however, at least in part, to the higher operating temperature employed. A comparison of the two media may be made from the data of Table VI.

TABLE VI
COMPARISON OF LIQUID PETROLATUM AND TETRALIN AS SUSPENDING MEDIA

Coal	Liquid petrolatum			Tetralin		
	Oils and gas	Water	Total	Oils and gas	Water	Total
Conversions on basis of dry coal						
A	7.1	0.0	7.1	10.8	0.0	10.8
B	9.3	0.0	9.3	32.3	0.0	32.3
C	38.0	2.8	40.8	64.1	0.5	64.6
D	37.7	0.0	37.7	73.4	0.1	73.5
E	44.1	3.8	47.9	74.7	2.3	77.0
F	45.9	4.4	50.3	79.0	1.0	80.0
G	47.8	7.8	55.6	69.7	10.8	80.5
H	53.9	7.1	61.0	72.6	8.7	81.3
J	54.5	7.3	61.8	79.0	7.4	86.4
K	53.8	9.2	63.0	72.9	13.4	86.3
L	36.9	10.0	46.9	67.8	15.2	83.0
M	50.9	6.6	57.5	77.7	10.0	87.7
N	60.3	14.3	74.6	72.9	15.1	88.0
Conversions on basis of dry, ash-free coal						
A	8.0	0.0	8.0	12.2	0.0	12.2
B	10.1	0.0	10.1	34.9	0.0	34.9
C	42.5	3.1	45.6	71.7	0.6	72.3
D	43.6	0.0	43.6	84.9	0.1	85.0
E	49.9	4.3	54.2	84.1	2.9	87.0
F	52.7	5.0	57.7	90.9	1.1	92.0
G	53.8	8.8	62.6	78.6	12.1	90.7
H	59.1	7.8	66.9	79.7	9.6	89.3
J	60.1	8.0	68.1	86.9	8.2	95.1
K	59.9	10.0	69.9	80.5	15.2	95.7
L	40.4	11.0	51.4	74.5	16.7	91.2
M	56.1	7.3	63.4	85.7	11.0	96.7
N	66.0	15.6	81.6	79.9	16.3	96.2

The columns in Table VI are self-explanatory and the data serve to show quite clearly the effects of the two media. A rapid comparison may be made by consulting Fig. 6, in which the degree of hydrogenation is shown graphically. In this diagram the conversion of coal in all cases represents percentage converted to gas, oil and water, and is calculated from the residual solid material. The large discrepancy in the results for Coal L in the petrolatum series has been mentioned earlier, and is due to the high temperature at which hydrogenation took place.

The ultimate analyses of the dry, ash-free coals also have been recorded in Fig. 6. It will be seen that, in general, the extent of hydrogenation parallels roughly the oxygen content of the coal, and changes inversely with the carbon content. This fact was recognized by Bergius (2), who, in this connection,

predicted that coals containing more than 85% carbon were not amenable to hydrogenation. Thus, of this series, Coals A-E inclusive should not be susceptible to hydrogenation. However, it was found that Coals C, D and E were quite susceptible to hydrogenation and appreciable reduction of Coals A and B also occurred.

The effective action of tetralin as a medium compared to other substances has been attributed previously (3) to a hydrogen carrying action. These earlier results showed clearly that tetralin can hydrogenate coal in the absence of free hydrogen, with the resulting formation of naphthalene. In fact, naphthalene is produced in amounts that increase with a decreasing supply of gaseous hydrogen. It is reasonable to assume that the mechanism

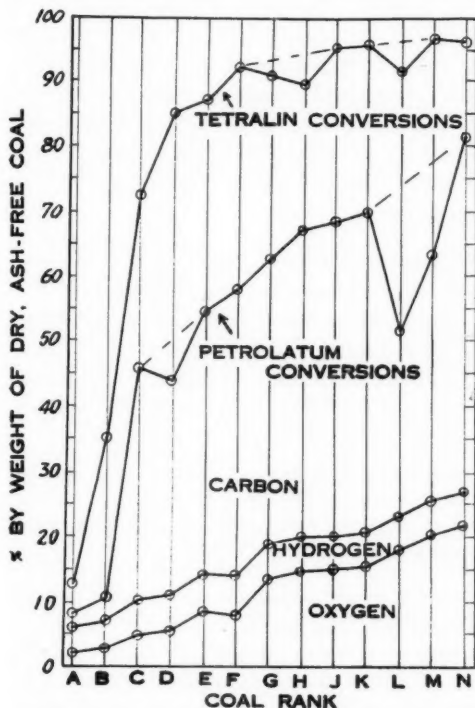


FIG. 6. Coal conversion, rank, and ultimate analysis on dry ash-free basis.

is the same in all cases, that the tetralin hydrogenates the coal and that the hydrogen reduces the resulting naphthalene to tetralin.

It has been fairly well established that, in destructive hydrogenation processes, four reactions predominate; a thermal decomposition of complex bodies to form unsaturated fragments, a hydrogenation or stabilization of these fragments, a decomposition and polymerization of these fragments to form coke and gas and hydrogenation of phenolic bodies with the production of water. Waterman and Perquin (13, 14) in working with paraffin wax were led to the theory that the function of the hydrogen was, primarily, that of stabilizing unsaturated fragments by prevention of dehydrogenation. The fragments were themselves stable. Kling and Florentin (8) and Tropsch (12) do not support this and suggest that the hydrogen reduces the unsaturated fragments to form saturated stable bodies. The hydrogenation equilibrium

is favored by low temperatures, and the decomposition and polymerization reactions resulting in coke and gas formation are favored by high temperatures. Moreover, the latter reactions tend to go to completion (7, 14). The function of the catalyst may be said to be the promotion of decomposition at low temperatures at which hydrogenation can proceed to an extent sufficient to reduce all or most of the unsaturated fragments.

The evidence of the work in this laboratory on tetralin and other media is in substantial agreement with the second mechanism. A significant modification in the mechanism is suggested, however. It is suggested that the function of the medium is the reduction of the unsaturated fragments or bodies, and the function of the hydrogen is the maintenance of the medium in the reduced state.

The Oxygenated Compounds in the Hydrogenation of Coal

Parr and Hadley (11) investigated the oxidation of coal and found that the combined oxygen was liberated as carbon dioxide upon thermal decomposition of the coal. It is thus reasonable to suppose that carbon dioxide is a product, to some extent, of thermal decomposition rather than of the specific action of hydrogen. This would account for the production of carbon dioxide in comparable amounts in the two series of experiments.

The formation of water is due in a large measure to hydrogenation of phenolic bodies in the coal (12). Examination of Table VI reveals that in general water is produced to a greater extent in the tetralin series. Two theories may be suggested to account for this.

Increased water formation in the tetralin series may be attributed to the higher temperature of operation throughout, resulting in a decreased stability of the phenolic substances. This theory is substantiated by the excessive water yields reported in those experiments of the petrolatum series in which the temperature of the reaction chamber rose above 430° C. For example, Experiment 164 with Coal K-310 was out of control and the temperature rose to 442° C. The water yield in this case was 4.6%. In Experiment 166 with Coal L-311 the temperature rose to 470° C. and the yield of water was 5.0%. Experiments with other domestic coals resulted in water yields averaging 3.5% (neglecting Coal N-312, of lignitic character). In these experiments the temperature did not rise above 430° C.

The alternative theory may be stated with some evidence in its favor. It is the view that excessive water yields are produced by hydrogenation of phenolic bodies which would otherwise remain unattacked, the action being attributed to the efficient manner in which tetralin itself will act as a hydrogenating agent. In view of the fact that operation at 450° C. caused a water yield of 8.7% in Experiment 165 on Coal L-311 of the tetralin series, a yield much higher than the 5.0% reported in the corresponding liquid petrolatum experiment in which the temperature reached 470° C., it may be concluded that tetralin has a specific action.

It is probable that both temperature and medium affect the water yield. Unfortunately, definite information would depend on experiments which have not been made, *viz.*, experiments involving equal temperatures of operation for the two media, and ultimate analyses.

The mechanism of reactions involving the production of carbon monoxide is more obscure, and no justifiable conclusions may be drawn from the data presented. It may be remarked, however, that reduction of carboxyl groups by successive stages would produce aldehydes which, according to Hurd (6), decompose readily to give carbon monoxide and a hydrocarbon. Such a source is not improbable and would fit the observed facts.

References

1. AREND, J. P. Int. Conf. on Bit. Coal, 2 : 485-490. 1928.
2. BERGIUS, F. Int. Conf. on Bit. Coal, 102-131. 1926.
3. BOOMER, E. H. and SADDINGTON, A. W. Can. J. Research, 4 : 517-539. 1931.
4. BOOMER, E. H. and SADDINGTON, A. W. Can. J. Research, 12 : 825-839. 1935.
5. HALL, C. C. Fuel Science Practice, 12 : 76-93. 1933.
6. HURD, C. D. The pyrolysis of carbon compounds. The Chemical Catalog Co., New York. 1929.
7. KISS, S. A. Ind. Eng. Chem. 23 : 315-318. 1931.
8. KLING, A. and FLORENTIN, M. D. Int. Conf. on Bit. Coal, 2 : 523-541. 1928.
9. LAYNG, T. E. and HATHORNE, W. S. Ind. Eng. Chem. 17 : 165-167. 1925.
10. LUSH, E. J. J. Soc. Chem. Ind. 46 : 454T-456T. 1927.
11. PARR, S. W. and HADLEY, H. F. Fuel, 4 : 31-38; 49-55; 111-118. 1925.
12. TROPSCH, H. Fuel, 11 : 61-66. 1932.
13. WATERMAN, H. I. and PERQUIN, J. N. J. J. Inst. Petroleum Tech. 10 : 842. 1924.
14. WATERMAN, H. I. and PERQUIN, J. N. J. J. Inst. Petroleum Tech. 11 : 36-60; 374-378. 1925.
15. WILSON, H. A. Proc. Roy. Soc. (Lond.) A124 : 16-45. 1929.

STUDIES ON LIGNIN AND RELATED COMPOUNDS

XII. METHANOL LIGNIN¹BY FRITZ BRAUNS² AND HAROLD HIBBERT³

Abstract

Methanol lignin was prepared by extracting spruce wood meal with absolute methyl alcohol, using hydrochloric acid as catalyst. In five small, bomb-tube experiments, methanol lignin preparations having the same methoxyl content (about 21.6%) were obtained, the product in each case being apparently homogeneous. The methanol lignin was acetylated, partially methylated by treatment with diazomethane, and fully methylated with dimethyl sulphate and sodium hydroxide. From the elementary analyses and the ratio of methoxyl in the original methanol lignin to that in the diazomethane-methylated compound a formula for the smallest building unit of the methanol lignin and for the native lignin can be derived. The latter is represented by the empirical formula $C_{47}H_{52}O_{16}$, or, expanded, $C_{42}H_{32}O_8(OCH_3)_5(OH)_3$.

Introduction

The method of isolating lignin from wood by means of hydroxylic compounds in presence of catalysts, such as hydrochloric acid, has been used by a number of investigators during the past 15 years. Grüss (11, 12) was apparently the first to show that lignin could be isolated from wood by heating the latter with alcohol and hydrochloric acid. Later, Hägglund (13-15) applied this same principle, and using a variety of alcohols (methyl, ethyl, amyl) claimed to show that the resulting lignin derivatives were "acetal" derivatives, although no definite proof of this theory was submitted.

Hibbert and co-workers (16, 17) carried out a series of investigations on "glycol lignin" and "glycol monomethyl ether lignin" in which the extraction media were glycol and glycol monomethyl ether respectively. The first method was used independently by Rassow (18-20), and the second, by Fuchs (9). Friedrich and co-workers (7, 8) and Campbell (3) employed ethyl alcohol as the extraction medium. In all cases a product is obtained which contains, depending on the solvent used, the alkyl or the aryl group in ether-like combination with the lignin. In the case of both the lower aliphatic alcohols and of glycol or glycol monoalkyl ethers, the methoxyl value as determined by the standard procedure is influenced by the presence of these groups; on the other hand, the use of phenol as extraction medium gives rise to more complicated lignin derivatives formed as the result of nuclear condensation of the phenol with the lignin molecule (2). In view of this, it seemed advisable to investigate further the use of methyl alcohol as proposed previously by Friedrich (7, 8). The reaction between the methyl alcohol and lignin would be indicated by the higher value of the methoxyl content. The mechanism of the reaction is not clear (4, p. 125).

¹ Manuscript received March 21, 1935.

Contribution from the Pulp and Paper Research Institute, McGill University, Montreal, Canada, with financial assistance from the Canadian Pulp and Paper Association.

² Research Chemist and holder of the Canadian Pulp and Paper Association Fellowship.

³ Professor of Industrial and Cellulose Chemistry, McGill University.

Hägglund (13) has suggested that the products are acetals. Since, however, they do not undergo hydrolysis with dilute mineral acids, it is evident that this view is incorrect. In an earlier investigation (10, 16) it was found that, on extracting spruce wood meal with ethylene glycol monomethyl ether, the methoxyl content of the resulting lignin derivative, calculated on the basis of a molecular weight of about 850, had increased by an amount corresponding to approximately one methoxyl group, thus indicating that at least one molecule of glycol monomethyl ether had reacted with the lignin.

As shown in the present paper, extraction of spruce wood meal with absolute methanol yields a methanol lignin in which an additional methoxyl group has been introduced, so that on treatment with hydriodic acid an additional amount of methyl iodide is evolved.

When bone-dry wood meal, previously freed of fats, waxes, resins and water-soluble carbohydrates, is heated in a bomb tube with methyl alcohol containing 2% of hydrogen chloride in a tilting-oven at 85–90° C. for about 100 hr., 50% of the wood meal dissolves and from this a methanol lignin with a methoxyl content of 21.6% can be isolated. Lignin which has been isolated according to Freudenberg's method (5, 6) and which may be considered as closely related to unchanged native lignin, has a methoxyl content of 17.4% (4, p. 125). The increase of approximately 4% in the methoxyl content of methanol lignin, as compared with the methoxyl content of Freudenberg lignin, would seem to be due to the entrance of new methoxyl groups into the lignin molecule as a result of the reaction between the lignin and the methanol.

Methanol lignin is soluble in sodium hydroxide solution, from which it is reprecipitated on the addition of a mineral acid or even carbon dioxide, indicating the presence of a phenolic hydroxyl group. This is confirmed by the behavior of the methanol lignin towards diazomethane. On treatment with this reagent in dioxane solution a strong evolution of nitrogen takes place. The solution changes in color from dark brown to a light brownish-yellow, and a methylated product insoluble in sodium hydroxide and having a methoxyl content of 24.8% is formed. In addition to this weakly acidic hydroxyl group, other hydroxyl groups are present as shown by the acetylation of the original methanol lignin and of its diazomethane-methylated derivative. The acetyl derivatives are no longer soluble in alkali solution.

The presence of free hydroxyl groups in methanol lignin is also shown by the formation of a methylated derivative on treatment with dimethyl sulphate and sodium hydroxide, the fully methylated methanol lignin formed by this treatment having a methoxyl content of 32.3%.

Based on the original methoxyl values of the methanol lignin (21.6%) and the diazomethane-methylated product (24.8%), the number of methoxyl groups in the smallest lignin building-unit can be calculated if it be assumed that only one methoxyl group is formed as a result of methylation with

diazomethane. If x represents the molecular weight of the original methanol lignin and y the number of the methoxyl groups, the percentage of methoxyl is given by

$$\frac{31.02 \times y \times 100}{x} = 21.6,$$

and for the diazomethane-methylated methanol lignin the value is represented by

$$\frac{31.02 (y + 1) \times 100}{x + 14} = 24.82,$$

from which y is found to be 6.05, and x to be 861.

In other words, methanol lignin contains (on the basis of one new methoxyl group formed by the action of diazomethane) six, and the diazomethane-methylated product seven, methoxyl groups, a result in agreement with that shown in an earlier paper (1). It must, however, be emphasized that these calculations are based on the assumption that the original methanol lignin is a homogeneous product. In the bomb-tube experiments described below, in which only small amounts could be prepared, a *single* product only, insoluble in ether, was obtained. Owing to lack of sufficient material no other fractionation experiments could be carried out. As will be shown in a later paper, however, when methanol lignin is prepared on a larger scale in an autoclave, the crude methanol lignin can be separated into two fractions, namely, an ether-insoluble and an ether-soluble, having methoxyl contents of 21.5 and 24.4% respectively. A detailed examination of the two products, their acetylated diazomethane-methylated and fully methylated compounds, is at present being carried out with the object of obtaining more precise information regarding the size of the methanol lignin building-unit.

The formula for methanol lignin is therefore, as shown in the earlier paper, $C_{42}H_{32}O_6(OCH_3)_6(OH)_4(OCH_3)_5$, and for native lignin, $C_{42}H_{32}O_6(OCH_3)_5(OH)_5$.

Experimental

Preparation of Methanol Lignin

Spruce wood meal (25 gm., 100 mesh), dried to constant weight under reduced pressure at 50° C. over phosphorus pentoxide, was heated in a sealed glass bomb tube with 200 cc. of absolute methanol containing 2% of anhydrous hydrochloric acid in a tilting oven at 90–100° C. for 80 hr. The tube was cooled to –15°C. When the tube was opened, a pronounced evolution of gas, presumably methyl chloride, or dimethyl ether, was observed. A slight smell of formaldehyde was also detectable. The reaction product was centrifuged, the residual wood meal washed with a mixture of acetone and methanol (1 : 1) and dried in a desiccator over sulphuric acid. The weight was 12.3 gm., indicating that 50% of the original wood meal had been dissolved. The combined methanol and acetone solutions were concentrated under reduced pressure to a volume of about 20 cc. and then added dropwise in a very fine stream to 500 cc. of well stirred distilled water containing a trace of sodium bicarbonate. The lignin precipitated, in general, as a flocculent material but

occasionally remained in colloidal solution. In the latter case it was stirred with a few drops of concentrated sodium sulphate solution which brought about coagulation. The methanol lignin was separated by centrifuging, and finally by filtering through a Büchner funnel. It was washed with distilled water until it was free from sulphate and no longer reduced Fehling's solution. The slimy, chocolate-brown colored product was dried in a desiccator over sulphuric acid. Yield, 1.8 gm. or 25% of the total lignin present in the original spruce meal. Analysis of the product from three different experiments gave OCH_3 , 22.0, 21.8, 21.6%, respectively.

Purification of the Methanol Lignin

The methanol lignin was dissolved in sufficient anhydrous dioxane to form a 10% solution and then reprecipitated by adding the solution dropwise to vigorously stirred anhydrous ether. The product was washed twice with ether, then three times with petroleum ether, allowed to stand overnight in the final petroleum ether wash liquor, filtered, and dried in a desiccator over sulphuric acid. A sample for analysis was dried over phosphorus pentoxide at 2 mm. and 110° C. to constant weight. Found: OCH_3 , 21.5%. This product was again purified from dioxane and ether. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6$ (OCH_3)₆(OH)₄, [886.4]:—C, 64.9; H, 6.1; OCH_3 , 21.0%. Found: C, 65.12, 65.25; H, 6.02, 6.14; OCH_3 , 21.6%.

Methanol lignin is a finely divided buff-colored powder, soluble in dioxane, acetone, methyl and ethyl alcohols, and in dilute sodium hydroxide. It is precipitated from the last-named solution by mineral acids and also by carbon dioxide.

The mother liquor from the methanol-water precipitation was evaporated under reduced pressure to a thick syrup. This was dissolved in distilled water, the small amount of pale brown precipitate which separated out removed by filtration through charcoal, and the aqueous solution evaporated under reduced pressure. The yellowish brown syrup finally obtained was then dried in a vacuum desiccator for several days over solid sodium hydroxide. About 10 gm. of the yellowish brown syrup was obtained in each experiment. This product reduced Fehling's solution only slightly but very strongly after hydrolysis with dilute hydrochloric acid. In the latter case a slight brown flocculent precipitate separated out. After it had been filtered and dried its methoxyl content was 17.5%.

The dioxane-ether mother liquor obtained from the first purification of the methanol lignin was only slightly colored. The solvent was removed by evaporation under reduced pressure, the brownish residue dissolved in about 2 cc. of dioxane and this solution added dropwise to well stirred petroleum ether. Only a very slight precipitate was obtained. This was not investigated further.

The residual methanol-extracted wood meal from three such experiments, representing 50% of the original wood meal used, was dried and analyzed for methoxyl, lignin and cellulose. The methoxyl content, 6.11%, is nearly

50% higher than that of the original wood meal (4.4%), indicating that during the extraction with methyl alcohol and hydrogen chloride a partial methylation had taken place.

A lignin determination showed 26.9% as compared with 29.4% prior to extraction, and a cellulose content of 66.9% was found, as compared with 58.6% in the original wood meal. An extraction of methanol lignin carried out in an open flask at 66° C. resulted in a poorer yield of a crude methanol lignin (OCH_3 , 22.7%).

Acetylation of Purified Methanol Lignin

One gram of purified methanol lignin (OCH_3 , 21.6%) was dissolved in a mixture of 5 cc. of dry pyridine and 3 cc. of acetic anhydride; the product was allowed to stand at room temperature for 48 hr., and then poured on to ice. The brown precipitate was filtered, washed and dried over sodium hydroxide and sulphuric acid in a vacuum desiccator. It was then dissolved in dioxane, and the solution was centrifuged, filtered and the lignin precipitated by adding the solution dropwise to well stirred anhydrous ether. It was purified further by dissolving it in dry benzene and adding the filtered solution drop by drop to petroleum ether (60–70° C.) with vigorous stirring. The precipitated product was washed first with petroleum ether (b.p. 60–70° C.) then with low-boiling petroleum ether (b.p. 30–50° C.). The product isolated by centrifuging was dried in a vacuum desiccator over sulphuric acid. Yield, 1.2 gm. Prior to analysis it was dried in an Abderhalden oven at 78° C. and 2 mm. to constant weight. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_6(\text{OCOCH}_3)_4$, [1054.5]:—C, 63.9; H, 5.9; OCH_3 , 17.6%. Found:—C, 64.46, 64.20; H, 5.65, 5.77; OCH_3 , 17.8%. The acetylated methanol lignin is soluble in benzene, acetone, dioxane and methyl and ethyl alcohols, but insoluble in ether, petroleum ether, water and dilute sodium hydroxide solution.

Methylation of Methanol Lignin with Diazomethane

Two grams of purified methanol lignin was dissolved in 20 cc. of dioxane and the diazomethane prepared from 10 cc. of nitrosomethyl urethane was passed into the solution at 5° C. The reaction product was allowed to stand for 18 hr. at room temperature and was then heated to 50° C. for 15 min. This brought about the separation of a slimy precipitate which, on centrifuging, floated on the surface of the solution. After filtration, the clear solution was added dropwise to well stirred dry ether. The methylated methanol lignin separated out as a very fine light-brown powder. This was centrifuged, redissolved in dioxane and again precipitated with ether. The product was washed with ether and then twice with petroleum ether. Yield, 1.7 gm. The low yield was due to losses incurred in filtration. The product prior to analysis was dried to constant weight in an Abderhalden oven at 110° C. and 2 mm. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_7(\text{OH})_3$, [900.4]:—C, 65.3; H, 6.2; OCH_3 , 24.1%. Found:—C, 66.15, 66.44; H, 6.30, 6.41; OCH_3 , 24.9, 24.9, 24.6%.

Methanol lignin methylated with diazomethane shows a degree of solubility in organic solvents similar to that found for the original methanol lignin, but differs however from the latter in that it is insoluble in dilute sodium hydroxide.

In a second experiment the yield of purified product was quantitative and the same methoxyl value was obtained on analysis.

Acetylation of Methanol Lignin Premethylated with Diazomethane

Methanol lignin (2.8 gm.), premethylated with diazomethane, was dissolved in 15 cc. of pyridine and 10 cc. of acetic anhydride added. After standing for 48 hr. at room temperature the mixture was poured on to ice, the precipitated product filtered off, and dried in a vacuum desiccator over sulphuric acid and sodium hydroxide. It was purified by solution in dioxane and precipitation with ether. After it had been washed several times with petroleum ether, the product was dried at 100° C. and 2 mm. pressure for 24 hr. Yield, 3 gm. The acetylated product shows a behavior similar to that of the acetylated methanol lignin with respect to organic solvents. Calcd. for $C_{42}H_{32}O_6(OCH_3)_7(OCOCH_3)_3$, $[1026.5]:-OCH_3$, 21.1%. Found: $-OCH_3$, 21.4, 21.5%.

Preparation of the Fully Methylated Methanol Lignin by Simultaneous Deacetylation and Methylation

Methanol lignin (2.6 gm.), methylated with diazomethane and then completely acetylated, was dissolved in 30 cc. of acetone and then subjected to a combined deacetylation and methylation treatment at 40° C. with 30 cc. of dimethyl sulphate and 65 cc. of sodium hydroxide solution (30%). The reagents were added in five portions at intervals of 30 min., and the mixture was kept slightly alkaline. The acetone was then distilled off, whereupon the reaction product separated as a sticky mass, which, on cooling, became solid. It was filtered off, ground in a mortar with water in order to remove the sodium sulphate, redissolved in acetone and remethylated, using the same amount of reagents and under the same conditions. The isolated product was purified by dissolving in dioxane and precipitating with dry ether. It separated as a fine light-brown powder, which was centrifuged, washed with ether, then twice with petroleum ether and dried in a desiccator over sulphuric acid. Yield, 2.3 gm. Prior to analysis the product was dried at 110° C./2 mm. Calcd. for $C_{42}H_{32}O_6(OCH_3)_{10}$, $[942.7]:-C$, 66.2; H, 6.6; OCH_3 , 32.9%. Found: $-C$, 66.36, 66.05; H, 6.64, 6.53; OCH_3 , 32.3%.

On repeating the methylation no increase in the methoxyl content was found. Also, treatment of this product with pyridine and acetic anhydride brought about no change in methoxyl value, indicating absence of free hydroxyl groups.

The fully methylated methanol lignin is soluble in acetone, methyl and ethyl alcohols and benzene, insoluble in ether, petroleum ether, water and sodium hydroxide. On heating with dilute sulphuric acid (5%) at 100° C. in aqueous acetone solution, no change in the methoxyl content takes place, indicating the absence of any readily hydrolyzable methoxyl groups.

References

1. BRAUNS, F. and HIBBERT, H. J. Am. Chem. Soc. 55 : 4720-4727. 1933.
2. BUCKLAND, I. K., BRAUNS, F. and HIBBERT, H. Can. J. Research, B, 13 : 61. 1935.
3. CAMPBELL, W. G. Biochem. J. 23 : 1225-1232. 1929.
4. FREUDENBERG, K. Tannin, Cellulose, Lignin. J. Springer, Berlin. 1933.
5. FREUDENBERG, K., HARDER, M. and MARKERT, L. Ber. 61 : 1760-1765. 1928.
6. FREUDENBERG, K., ZOCHER, H. and DÜRR, W. Ber. 62 : 1814-1823. 1929.
7. FRIEDRICH, A. and BRÜDA, B. Monatsh. 46 : 597-610. 1925.
8. FRIEDRICH, A. and DIWALD, J. Monatsh. 46 : 31-46. 1925.
9. FUCHS, W. Ber. 62 : 2125-2132. 1929.
10. GRAY, K. R., KING, E. G., BRAUNS, F. and HIBBERT, H. Can. J. Research, B, 13 : 35-47. 1935.
11. GRÜSS, J. Ber. botan. Ges. 38 : 361-368. 1921.
12. GRÜSS, J. Ber. botan. Ges. 41 : 48-52. 1923.
13. HÄGGLUND, E. and ROSENQUIST, T. Biochem. Z. 179 : 376-383. 1926.
14. HÄGGLUND, E. and URBAN, H. Cellulosechemie, 8 : 69-71. 1927.
15. HÄGGLUND, E. and URBAN, H. Cellulosechemie, 9 : 49-53. 1928.
16. HIBBERT, H. and MARION, L. Can. J. Research, 2 : 364-375. 1930.
17. HIBBERT, H. and ROWLEY, H. J. Can. J. Research, 2 : 357-363. 1930.
18. RASSOW, B. and GABRIEL, H. Diss. Leipzig. 1928.
19. RASSOW, B. and GABRIEL, H. Cellulosechemie, 12 : 227-235; 249-254; 290-295; 318-320. 1931.
20. RASSOW, B. and WAGNER, K. Diss. Leipzig. 1931.

STUDIES ON LIGNIN AND RELATED COMPOUNDS

XIII. THE STRUCTURE AND PROPERTIES OF GLYCOL LIGNIN¹

By K. R. GRAY², E. G. KING³, FRITZ BRAUNS⁴ AND HAROLD HIBBERT⁵

Abstract

Lignin was extracted from spruce wood meal with ethylene glycol containing (a) 0.05% and (b) 0.2% hydrogen chloride. On purification the two glycol lignins were found to contain 16.9% OCH_3 and 62.8% C., and 16.5% OCH_3 and 64.7% C. respectively. The aqueous glycol mother liquor was found to contain a soluble lignin-carbohydrate compound. The glycol lignin could be separated into a chloroform-insoluble and a chloroform-soluble fraction, each having the same chemical composition and yielding the same methylated products. From the glycol lignin, purified by means of dioxane-ether, acetylated and methylated derivatives were prepared, as were also trityl derivatives of glycol lignin and premethylated glycol lignin.

The introduction of three trityl groups indicates the presence of three primary alcohol groups in the original lignin. Glycol lignin can be both partially and completely demethylated by use of hydriodic acid. The effect of the glycol radical on the methoxyl value in the Zeisel determination was studied and an equation derived for the correction of the methoxyl value. The bearing of the results on the formula proposed previously (1) for methanol lignin is discussed.

Introduction

It has been shown in previous communications (3, 4) that lignin can be extracted from wood with ethylene glycol in the presence of small amounts of hydrogen chloride as catalyst. Lignin derivatives isolated in this way were originally thought to be acetals but are now regarded as ethers of the lignin and the alcohol (1).

In order to determine how much lignin can be extracted from the wood in this way, four successive extractions were carried out with ethylene glycol containing 0.05% hydrogen chloride, and the progress of the extraction followed by analysis of the wood meal residues. The percentage of lignin extracted and that isolated after each extraction together with the corresponding results given by Hibbert and Marion are shown in Table I.

The process of preparing glycol lignin involves only slight mechanical losses, so that the large lignin losses (almost 50% in the first and second extractions) (Table I) must have been due to lignin remaining in the aqueous solution when the glycol lignin was precipitated by pouring the glycol solution

¹ Manuscript received March 25, 1935.

Contribution from the Pulp and Paper Research Institute, McGill University, Montreal, Canada, with financial assistance from the Canadian Pulp and Paper Association. This paper was constructed from the theses presented by K. R. Gray and E. G. King, in October 1934, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Postgraduate student, McGill University, and holder of a bursary under the National Research Council of Canada, 1931-1932. Demonstrator, Department of Chemistry, McGill University, 1932-1934.

³ Postgraduate student, McGill University, and holder of International Paper Company Fellowship.

⁴ Research Chemist and holder of Canadian Pulp and Paper Association Research Fellowship.

⁵ Professor of Industrial and Cellulose Chemistry, McGill University.

TABLE I
COMPARISON OF AMOUNTS OF LIGNIN EXTRACTED AND ACTUALLY RECOVERED

	Lignin extracted*		Crude lignin isolated*		Purified lignin isolated*
	Gray	Hibbert and Marion†	Gray	Hibbert and Marion	Gray
In first extraction	46.53	36.7	24.35	20.5	22.0
In second extraction	28.89	12.7	14.6	8.2	13.8
In third extraction	3.06	—	3.3	—	2.95
In fourth extraction	2.38	—	2.2	—	1.9
Total of all extractions	80.86	49.4	44.45	28.7	40.65

*Calculated as percentage of original lignin in wood meal.

†The figures are calculated from results given by Hibbert and Marion (3) for extractions carried out under conditions identical with those employed by the authors; namely, the use of anhydrous glycol containing 0.05% hydrogen chloride at a temperature of 107–109° C. for eight hours.

into water. This loss may be due either to a solubility effect of the water-glycol mixture, or to the presence of a soluble lignin-carbohydrate complex present in the wood or formed during the extraction.

The possible role played by the "soluble lignin" in the aqueous glycol mother liquor was investigated by studying the effect of concentrating the glycol lignin extract prior to precipitation with water. It was found that the decrease in loss after concentration was only 32.9% of that occurring when the glycol extract was not concentrated.

It was possible to isolate from the aqueous glycol mother liquor a lignin compound in a small yield by precipitating with basic lead acetate. This product appeared to be a compound of lignin with a carbohydrate. After careful decomposition with dilute sulphuric acid, a brown solution was obtained which reduced Fehling's solution only when hydrolyzed with hydrochloric acid, yielding a water-insoluble precipitate with a methoxyl content of 14.2%, but soluble in dioxane and dilute sodium hydroxide solution. The colorless filtrate from the hydrolysis reaction reduced Fehling's solution very strongly. Acetylation of the lead salt gave a product with a large acetyl value and a correspondingly low methoxyl content.

Glycol lignin, purified by adding its dioxane solution to ether, thus precipitating a fine powder, has a methoxyl content of 16.9%, the same value as that found first by Rassow and Gabriel (5), and this value did not change on further purification with other solvents or on hydrolysis. Rassow and Gabriel (5) assumed that their glycol lignin did not contain bound glycol. In order to settle this question, since the presence of glycol may affect the methoxyl determinations, several attempts were made to hydrolyze off the glycol radical and to isolate the glycol, but they were unsuccessful. The proof of the presence of glycol was finally obtained indirectly by using glycol monomethyl ether instead of glycol as extraction medium. The glycol mono-

methyl ether lignin so obtained had a methoxyl content of 20.5%, *i.e.*, approximately one methoxyl group more on the basis of a molecular weight of about 900.

In order to investigate the influence of the glycol radical on the methoxyl determination, such determinations were carried out on a number of known glycol derivatives of varying molecular weight, as shown in Table II. The

TABLE II
APPARENT METHOXYL VALUE GIVEN BY A GLYCOL GROUP

Compound	Found OCH ₃ , %	OCH ₃ due to presence of glycol radical, %	Glycol correction factor (% OCH ₃ mol. wt.)	OCH ₃ , % (K) calcd. from the mean correction factor and the mol. wt. $K = \frac{895}{\text{m.w.}}$
(a) Ethylene glycol (m.w. 62)	12.03 } 12.30 12.56 }	12.30	765	14.40
(b) Glycol dimethyl ether (m.w. 90)	77.21 } 77.56 77.90 }	8.67	780	9.90
(c) Glycol dicaprate (m.w. 370)	2.39 } 2.22 2.05 }	2.22	821	2.42
* (d) Tetra-acetyl glycol glucoside (m.w. 392)	1.83 } 1.93 2.03 }	1.93	757	2.29
(e) Glycol dimyristate (m.w. 482)	2.09 } 2.00 1.90 }	2.00	964	1.86
(f) Glycol dipalmitate (m.w. 542)	1.74 } 1.85 1.97 }	1.85	1003	1.65
(g) Glycol distearate (m.w. 595)	1.62 } 1.64 1.66 }	1.64	976	1.50
* (h) Hepta-acetyl glycol cellobioside (m.w. 680)	1.53 } 1.61 1.69 }	1.61	1095	1.22
			Mean 895	

*These two products were prepared for us by Dr. M. L. Wolfrom, The Ohio State University, to whom we wish to express our best thanks for this kindness.

methoxyl value did not decrease in exact proportion to the increase in molecular weight. By multiplication of the found methoxyl percentage due to glycol (Table II, Column 3) by the molecular weight of the respective glycol compound, a correction factor for each compound is obtained, and these factors (Column 4) are seen to vary within wide limits from 765 to 1095, the average value being 895.

Applying this value to glycol lignin with a molecular weight of 916, the correction is found to be 0.97%, that is the methoxyl value found would be

too high by this amount owing to the glycol in the lignin. In compounds with molecular weights greater than 1800, for example the phenol glycol lignins, the error is within the experimental error.

In any case it is evident that glycol lignin is not very suitable for studies on the structure of lignin when conclusions are to be based on the methoxyl determinations.

The carbon content of the glycol lignin obtained by extracting with 0.05% hydrogen chloride is 62.8%, while that obtained by the use of 0.2% hydrogen chloride is 64.5%, the latter value being also found by Rassow and co-workers. The methoxyl values do not show any difference, and the differences in carbon content disappear in the methylated and acetylated products.

As first shown by Rassow (2, 5, 7) glycol lignin can be separated into a chloroform-insoluble and a chloroform-soluble fraction, amounting to 75 and 25% respectively. The analytical data obtained for the two fractions and their methylated derivatives are shown in Table III and are seen to be in close agreement.

TABLE III
ANALYSIS OF CHLOROFORM FRACTIONATION PRODUCTS AND THEIR DERIVATIVES

Lignin derivative	Chloroform-insoluble fraction, %	Chloroform-soluble fraction, %
Untreated fraction	(OCH ₃) 16.95 C 62.61 H 6.22	(OCH ₃) 16.90 C 63.15 H 6.43
Methylated with diazomethane	(OCH ₃) 21.02	(OCH ₃) 21.36
Fully methylated	(OCH ₃) 32.00	(OCH ₃) 32.2

Using glycol lignin purified twice from dioxane and ether a series of glycol lignin derivatives was prepared. These comprised the acetyl, benzoyl, *p*-bromobenzoyl, *p*-nitrobenzoyl and *p*-toluene sulphonyl derivatives. On methylation of glycol lignin with diazomethane a derivative with a higher methoxyl content could be prepared which, as shown both by acetylation and benzoylation, still contained free hydroxyl groups. The complete methylation of glycol lignin was carried out by a simultaneous deacetylation and methylation of two products: (a) the fully acetylated glycol lignin, and (b) the acetylated glycol lignin previously methylated with diazomethane. In both experiments the same fully methylated product was obtained, with a methoxyl content of 31.4% for each product.

On treatment of glycol lignin, as well as of its diazomethane-methylated product, with trityl chloride in pyridine solution, trityl derivatives were obtained. The glycol lignin derivative was found to contain four trityl groups. There seems to be no doubt that one of these has replaced the hydrogen atom in the free hydroxyl of the glycol group, while a second has

been substituted for the hydrogen in the phenolic hydroxyl group. The diazomethane-methylated glycol lignin derivative contained only three trityl groups, since in this product the phenolic hydroxyl group has already been methylated by the diazomethane. In both cases there has been left one free hydroxyl group. On acetylation of these products the methoxyl value decreased somewhat, but on account of the high molecular weights in question no conclusions can be drawn from these latter experiments. The introduction of three trityl groups, however, into both the glycol lignin and the pre-methylated glycol lignin indicates the presence of three primary alcohol groups in the glycol lignin.

In an earlier paper by Brauns and Hibbert (1) a formula for glycol lignin was proposed which was derived from the analysis of the fully methylated, ether-insoluble glycol lignin and independent of that of the fully methylated ether-insoluble methanol lignin. The authors do not wish to be considered as regarding this formula as something definitely and finally proved. As long as there is no other more suitable formula for the glycol lignin unit available, that represented by $C_{42}H_{32}O_8(OCH_3)_5(OH)_4(OCH_2CH_2OH)$ will be adopted, and the calculated theoretical data given in the experimental part are based on it.

Attempts were made to demethylate glycol lignin and it was found that partial demethylation could be effected by heating its acetylated product with a mixture of acetic anhydride and glacial acetic acid saturated with hydrogen bromide at 120° C. for two hours. A product with 10.7% OCH_3 (equivalent to four methoxyl groups based on the foregoing formula) is obtained, while complete demethylation can be effected using hydriodic acid and phenol (Zeisel method). The product obtained in the latter case is soluble in dioxane and undoubtedly represents a phenol condensation product of the demethylated phenol lignin. Further investigations in this direction are in progress.

Experimental

Preparation of the Wood Meal

The wood used for the preparation of the lignin was a section of a log* from a freshly cut Northern Ontario white spruce tree about forty years old. The wood was converted to a fine flour by shaving, followed by grinding in a ball mill. The wood flour was screened and those portions passing through 65 and 100 mesh sieves used for the extractions. For analysis it was dried at 110° C./2 mm. over phosphorus pentoxide. Found: OCH_3 , 4.88; lignin, 28.94; cellulose, 51.90; acetyl, 1.26; ash, 0.25%.

After it had been dried, the wood meal was extracted for 24 hr. in a Soxhlet extractor with a mixture of equal parts by volume of benzene and 95% alcohol. The wood meal was then dried at 60° C. in a vacuum oven, and extracted with water at 50° C. and again dried at 60° C. in the vacuum oven.

*Kindly supplied by the Abitibi Power and Paper Company, Iroquois Falls, Ontario.

Extraction of the Wood Meal with Anhydrous Ethylene Glycol Containing 0.05% Hydrogen Chloride, and Isolation of the Crude Lignin

About 800 gm. of the extracted and well dried wood meal was heated for eight hours at 107–109° C. with 10 times its weight of anhydrous ethylene glycol containing 0.05% of anhydrous hydrogen chloride. The extraction was carried out in a 12 litre flask fitted with a motor-driven stirrer and thermometer, and during the process a stream of dry nitrogen was passed through the apparatus. The mixture was filtered, while hot, in a nitrogen atmosphere. The wood meal residue was washed thoroughly with hot glycol and the filtrate and washings combined. The glycol solution was then added in a fine stream, with stirring, to four times its volume of distilled water previously warmed to 50° C. The precipitated light-brown lignin was allowed to settle, washed four times with distilled water by decantation, filtered, again washed with distilled water and finally dried in a vacuum desiccator over sulphuric acid.

Each lot of the wood meal was extracted four times. After each extraction, the wood meal was washed with distilled water to remove the glycol, dried in the vacuum oven and analyzed.

Purification of the Crude Glycol Lignin

Crude, dry glycol lignin (20 gm.) was dissolved in 100 cc. of pure, warm dioxane. The solution was centrifuged, decanted from a small amount of residue and the latter extracted with another small portion of dioxane. The solution was filtered, concentrated to approximately 10% lignin content, and added dropwise to 1200 cc. of ether, stirred mechanically. The precipitated lignin was allowed to settle, the ether replaced by fresh ether and the lignin centrifuged. It was washed three times with dry ether, and again centrifuged. After washing in the same manner twice with dry petroleum ether (30–50° C.), it was dried in a vacuum desiccator over sulphuric acid and solid sodium hydroxide. The product so obtained was a buff-colored amorphous powder, the particles of which readily acquired electrostatic charges.

Two lots of purified glycol lignin from two different extractions were analyzed. Found:—Lot I: C, 62.8, 62.8; H, 6.5, 6.6; OCH₃, 16.7, 17.0%. Lot II: C, 62.8, 62.7; H, 6.0, 6.1; OCH₃, 16.8, 17.1, corr.* 15.9, 16.1%. Calcd. for C₄₂H₃₂O₆(OCH₃)₅(OCH₂CH₂OH)(OH)₄, [916.5]: C, 64.2; H, 6.2; OCH₃, 16.9%.

The glycol lignin was readily soluble in dioxane, glycol monomethyl ether, methyl and ethyl alcohols (90%), phenol, aqueous acetone, pyridine, and in dilute sodium hydroxide, partly soluble in chloroform and absolute acetone, and insoluble in benzene, ether, petroleum ether and water.

A third and fourth extraction of the same lot of wood meal yielded only a very small amount of glycol lignin with a lower methoxyl content (16.0%; corr. 15.0%).

*Owing to the presence of the glycol radical it is necessary to apply a correction factor (see Table II) to the experimental methoxyl values obtained.

Extraction of the Wood Meal with Glycol and 0.2% Hydrogen Chloride, and Isolation of the Crude Lignin

The extraction was carried out in the same manner but using 518 gm. of wood meal and five litres of ethylene glycol containing 0.2% hydrogen chloride.

The filtered glycol solution was divided into two equal parts. One was precipitated without further treatment, as described above, while the other was concentrated to one-quarter the volume. The non-concentrated solution yielded 30.0 gm. of crude, dry glycol lignin and the concentrated solution gave 34.1 gm.

The total residual wood meal from this experiment was washed once with glycol and was then washed thoroughly with four litres of methyl alcohol. The dissolved glycol lignin was isolated by concentrating under diminished pressure and adding the filtered solution dropwise to four times its volume of distilled water. Yield, 10.2 gm. The total yield of crude lignin was 74.4 gm. or 51.7% of the lignin contained in the original spruce wood meal.

The crude glycol lignin (64 gm.) obtained from both precipitations was purified by the method described above. Yield, 56 gm. Found: C, 64.6, 64.9; H, 6.0, 5.8%. Methoxyl determinations: After one precipitation from dioxane:—OCH₃, 16.6, 16.5%; corr., 15.6, 15.5%; after a second precipitation from dioxane:—OCH₃, 16.5%; corr., 15.5%; after precipitation from acetone:—OCH₃, 16.5, 16.4%; corr., 15.5, 15.4%. The product was, therefore, considered to be homogeneous with regard to methoxyl content. Calcd. for C₄₂H₃₂O₆(OCH₃)₅(OCH₂CH₂OH)(OH)₄, [916.5], C, 64.2; H, 6.1; OCH₃, 16.9%.

Extraction of Wood Meal with Ethylene Glycol Monomethyl Ether Containing 0.1% Hydrogen Chloride

The procedure was the same as that employed in the extraction of the wood meal with ethylene glycol.

From 241 gm. of dry wood meal (65 mesh) there was obtained 14.5 gm. crude, dry glycol monomethyl ether lignin, or 6.0% of the weight of the original wood meal.

The product was almost completely soluble in dioxane and was purified by adding the dioxane solution to ether, thus precipitating the product, using exactly the same technique as for glycol lignin. The purified product was a fawn-colored powder. Yield, 12.2 gm.

The product was soluble in dioxane, glycol monomethyl ether, alcohol (95%), chloroform, and insoluble in benzene, ether, water, sodium carbonate solution, etc. Found: OCH₃, 20.5%; corr. 19.5%. Calcd. for C₄₂H₃₂O₆(OCH₃)₅(OCH₂CH₂OCH₃)(OH)₄, [930.5]: OCH₃, 20.0%.

Acetylation of Glycol Lignin

Two grams of glycol lignin was dissolved in 10 cc. of dry pyridine and 5 cc. of acetic anhydride added. After it had stood for 24 hr. at room temperature, the clear solution was poured into ice water. The light-brownish precipitate

separating out was filtered, washed with distilled water, and dried over sulphuric acid and sodium hydroxide in a vacuum desiccator. It was purified by dissolving it in dry chloroform and pouring the solution, drop by drop, into absolute methyl alcohol, with vigorous stirring. The isolated product was redissolved in dioxane and precipitated again with ether. Yield, 2.2 gm. For the analysis it was dried in an Abderhalden over phosphorus pentoxide at 78° C./2 mm. Found: C, 62.16, 62.20, 62.37; H, 5.67, 5.68, 5.81; OCH₃, 14.1%; corr. 13.3%. Calcd. for C₄₂H₃₂O₆(OCH₃)₅(OCH₂CH₂OOCCH₃)(OCOCH₃)₄, [1126.5]: C, 62.9; H, 5.9; OCH₃, 13.8%. The acetylated glycol lignin is soluble in dioxane, chloroform, pyridine, glacial acetic acid and acetone; it is insoluble in methyl alcohol, ether, water and cold dilute sodium hydroxide solution.

Benzoylation of Glycol Lignin

Two grams of glycol lignin was dissolved in 15 cc. of dry quinoline and 6 cc. of benzoyl chloride added. After about one hour, crystallization of quinoline hydrochloride began and the product was allowed to stand at room temperature for 24 hr. The mixture was then poured into ice-cold sulphuric acid (5%), whereupon a sticky mass separated out. It was kneaded with water but did not become solid. The sticky, dark brown product was dissolved in chloroform, this solution washed with water, dilute sulphuric acid, 5% potassium bicarbonate solution and finally with water. It was then dried with calcium chloride and the benzoylated lignin precipitated by pouring the solution into dry methyl alcohol. It separated out as a fine, light-red powder which was dried over calcium chloride and phosphorus pentoxide. Yield, 2.8 gm. It was purified further by adding its dioxane solution dropwise to dry ether. For the analysis the product was dried at 100° C./2 mm. Found: C, 70.65, 70.75; H, 5.22, 5.08; OCH₃, 11.4; corr. 10.8%. Calcd. for C₄₂H₃₂O₆(OCH₃)₅(OCH₂CH₂OOCCH₃)₅(OOCCH₃)₄, [1436.6]: C, 70.1; H, 5.3; OCH₃, 10.8%. The benzoylated glycol lignin is soluble in chloroform, dioxane, pyridine and quinoline, but insoluble in ether, petroleum ether, methyl alcohol and water.

Preparation of p-Brombenzoyl Glycol Lignin

Two grams of glycol lignin was dissolved in 10 cc. of dry pyridine and a solution of 5 gm. of *p*-brombenzoyl bromide added. The mixture became hot and was cooled with ice water. It was then allowed to stand at room temperature for 24 hr., poured into ice water and the solid precipitate filtered off. After it had been dried in a desiccator over sodium hydroxide and sulphuric acid, it was purified by dissolving it in chloroform and adding the solution dropwise to well stirred dry ether. Yield, 2.2 gm. Further purification was effected by adding its dioxane solution dropwise to dry ether. Found: Br, 25.6; OCH₃, 7.1; corr. 6.7%. Calcd. for C₄₂H₃₂O₆(OCH₃)₅(OCH₂CH₂OOCCH₂Br)(OOCCH₂Br)₄, [1831.2]: Br, 21.5; OCH₃, 8.5%. Calcd. for* C₄₂H₃₂O₆(OCH₃)₄(OCH₂CH₂OOCCH₂Br)(OOCCH₂Br)₅, [2001.2]:

*In the case that one methoxyl group is split off and replaced by a *p*-brombenzoyl group.

Br, 24.0; OCH₃, 6.3%. The *p*-brombenzoyl glycol lignin is soluble in chloroform, dioxane, and acetone, but insoluble in ether, petroleum ether, methyl alcohol and water.

Preparation of p-Nitrobenzoyl Glycol Lignin

Two grams of glycol lignin was dissolved in 12 cc. of dry pyridine and mixed with a solution of 5 gm. of nitrobenzoyl chloride in 5 cc. of dry chloroform. After it had stood for 48 hr. at room temperature, the product was isolated in the same manner as in the case of the benzoyl glycol lignin. Yield, 2.2 gm. Found: OCH₃, 8.6%, corr. 8.1%. Calcd. for C₄₂H₃₂O₈(OCH₃)₅(OCH₂CH₂OOCC₆H₄NO₂)(OOCC₆H₄NO₂)₄. [1661.5]: OCH₃, 9.3%. The solubility relations of this compound are the same as those of benzoyl glycol lignin.

Preparation of Glycol Lignin p-Toluene Sulphonate

Two grams of glycol lignin was dissolved in 15 cc. of dry pyridine and 5 gm. of *p*-toluene sulphonyl chloride added. After a short time crystallization of pyridine hydrochloride began. The mixture was allowed to stand for 24 hr. at room temperature, then poured on to ice water, the ester separating as a very fine light-brown precipitate. This was filtered and dried in a vacuum desiccator over sulphuric acid and solid sodium hydroxide. The crude product was dissolved in dry chloroform and reprecipitated as in the case of acetyl lignin. It was purified by redissolving it in chloroform and adding the solution dropwise to ether. Yield, 3.1 gm. For the analysis the product was dried in an Abderhalden at 100° C./2 mm. Found: OCH₃, 8.5%, corr. 8.0%; S, 9.7, 9.65%. Calcd. for C₄₂H₃₂O₈(OCH₃)₅(OCH₂CH₂OSO₂C₆H₄CH₃)(OSO₂C₆H₄CH₃)₄, [1687.1]: OCH₃, 9.2; S, 9.5%. The glycol lignin toluene sulphonate is soluble in pyridine, chloroform and dioxane, but insoluble in ether, benzene, petroleum ether, water and dilute alkali solution.

Methylation of Glycol Lignin with Diazomethane

Two grams of purified glycol lignin was dissolved in 15 cc. of dry dioxane and a solution of diazomethane (prepared from 10 cc. of nitrosomethyl urethane) in 10 cc. of dry dioxane added at room temperature. A slow evolution of nitrogen occurred and the solution became lighter in color. The mixture was allowed to stand overnight at 15° C. The next day a similar quantity of the diazomethane solution was added and the mixture allowed to stand for another 24 hr. at room temperature. A small, slimy precipitate separated out. This was coagulated by heating the solution to 50° C. for 15 min.; the mixture was then centrifuged, filtered and the clear solution concentrated under reduced pressure. The methylated glycol lignin was isolated by pouring the solution into dry ether with vigorous stirring. The precipitated product was washed with dry ether and finally twice with petroleum ether. The diazomethane-methylated glycol lignin so obtained was a very finely divided, light-brown powder. Yield, 2.1 gm. Found: C, 63.90, 64.04; H, 6.31, 6.38; OCH₃, 21.2, 21.0%, corr. 20.2, 20.0%.

Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OH)(OH)_3$, [930.5]: C, 64.4; H, 6.3; OCH_3 , 20.0%. The methylated glycol lignin thus obtained is soluble in dioxane, pyridine, acetone, chloroform, methyl and ethyl alcohols, but insoluble in ether, petroleum ether, water and sodium hydroxide. A further methylation with diazomethane did not increase the methoxyl content. Found: OCH_3 , 21.0%, corr. 20.0%.

Acetylation of Glycol Lignin Premethylated with Diazomethane

Two grams of glycol lignin, premethylated with diazomethane, was acetylated under the same conditions as those described for glycol lignin. The product, after precipitation from water, was dried over sodium hydroxide and sulphuric acid, and purified by precipitating twice from dioxane and ether (light yellowish powder, yield quantitative). Found: C, 63.50, 63.50; H, 6.18, 6.00; OCH_3 , 17.5, 17.3%, corr. 16.7, 16.5%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OOCCH_3)(OOCCH_3)_3$, [1098.5]: C, 63.3; H, 6.0; OCH_3 , 16.9%. The acetyl derivative of the glycol lignin premethylated with diazomethane is soluble in acetone, dioxane, chloroform, but insoluble in ether, petroleum ether, water and dilute sodium hydroxide.

Benzoylation of Glycol Lignin Premethylated with Diazomethane

Two grams of glycol lignin premethylated with diazomethane was benzoylated using dry quinoline and benzoyl chloride, following the method used for glycol lignin. Yield, 2.5 gm. For the analysis it was dried at 100° C./2 mm. Found: C, 69.42, 69.58; H, 5.41, 5.41; OCH_3 , 13.8, 13.6, corr. 13.1, 12.9%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OOCCH_2C_6H_5)(OOCCH_2C_6H_5)_3$, [1346.6]: C, 69.5; H, 5.5; OCH_3 , 13.8%. Its solubility relations are similar to those of the benzoylated glycol lignin.

Preparation of the p-Toluene Sulphonyl Ester of the Glycol Lignin Premethylated with Diazomethane

This compound was prepared in the manner described for the corresponding compound of glycol lignin. Yield from 1 gm. of premethylated glycol lignin, 1.7 gm. Found: OCH_3 , 11.9, corr. 11.3%; S, 7.7, 7.83%. Calcd. for $C_{42}H_{32}O_6(OCH_3)_6(OCH_2CH_2OSO_2C_6H_4CH_3)(OSO_2C_6H_4CH_3)_3$, [1546.9]: OCH_3 , 12.0; S, 8.2%.

Complete Methylation of Glycol Lignin

This experiment was carried out in two different ways. In the first method the glycol lignin, premethylated with diazomethane, was used, but in the second, the acetylated glycol lignin was methylated by a simultaneous deacetylation-methylation process.

(a) Methylation of Glycol Lignin Premethylated with Diazomethane

Seven grams of premethylated lignin was acetylated as described previously and the acetylated product dissolved in 100 cc. of acetone. A simultaneous deacetylation and methylation was then carried out with 85 cc. of dimethyl sulphate and 175 cc. of 30% sodium hydroxide solution. The

reagents were added drop by drop in ten portions at intervals of 10–15 min. The temperature was maintained at 56° C. and the solution kept slightly alkaline throughout the process. After the last addition, the reaction mixture was stirred for a further two hours at the same temperature. The product then consisted of two layers which formed an emulsion on stirring. The acetone was distilled off, whereupon the mass separated out on the surface of the aqueous solution as a sticky mass, which solidified on cooling. It was filtered, washed with water and dried in a desiccator over sulphuric acid. This product was remethylated under the same conditions and the isolated product, after it had been dried in a desiccator, was extracted with acetone in a Soxhlet apparatus. The acetone solution was centrifuged, filtered and the product precipitated by pouring the solution into dry ether. A third methylation was then carried out under the same conditions and the product isolated as before. After purification by solution in acetone and precipitation with ether, the product was washed several times with petroleum ether. A sample was dried at 78° C./2 mm. Found: OCH_3 , 31.4%. This product was remethylated a fourth time in the same manner and purified. Yield, 5.5 gm. Found: C, 65.83, 65.41; H, 6.76, 6.86; OCH_3 , 31.3, corr. 30.4%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_9(\text{OCH}_2\text{CH}_2\text{OCH}_3)$, [986.5]: C, 65.7; H, 6.7; OCH_3 , 31.4%.

In order to find out whether this product was completely methylated, 0.5 gm. was submitted to an acetylation treatment with pyridine and acetic anhydride. A methoxyl determination of the isolated and purified product gave 31.57%. Since no decrease in the methoxyl content occurred, it is obvious that the product had been completely methylated. The fully methylated glycol lignin is soluble in acetone, pyridine, and dioxane, but insoluble in ether, petroleum ether, water and dilute sodium hydroxide solution.

(b) Methylation of Acetylated Glycol Lignin

Acetylated glycol lignin (6 gm.) was dissolved in 80 cc. of acetone and a combined deacetylation-methylation carried out with dimethyl sulphate and sodium hydroxide solution. Dimethyl sulphate (80 cc.) and sodium hydroxide (30%; 180 cc.) were added in five portions at intervals of 30 min. After the last addition, the reaction mixture was stirred for another hour. The methylated glycol lignin was isolated and purified as described under (a). After two methylations a sample was isolated, purified and dried at 78° C./2 mm. Found: OCH_3 , 31.9%. This product was remethylated under the same conditions, isolated and purified. Yield, about 75%. Found: C, 65.11, 65.53; H, 6.65, 6.76; OCH_3 , 31.4, corr. 30.4%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_9(\text{OCH}_2\text{CH}_2\text{OCH}_3)$, [986.5]: C, 65.7; H, 6.7; OCH_3 , 31.4%. These analytical data agree very well with those of the former experiment.

As indicated by the low yield and the color of the dioxane-ether solution, an appreciable amount of the lignin product must have remained dissolved in the mother liquor. This was isolated by completely evaporating the solvents, dissolving the light-brown viscous syrup in dry benzene and pre-

precipitating the product by adding the clear solution to well stirred petroleum ether. An orange-yellow powder separated. This was washed with fresh petroleum ether, filtered and dried over sulphuric acid. Found: OCH_3 , 32.7%.

In the same way the product from the diazomethane-ether mother liquor of Experiment (b) was isolated in a yield of 22%. Found: OCH_3 , 35.0%.

Preparation of a Trityl Derivative of Glycol Lignin

Glycol lignin (2.5 gm.) was dissolved in 15 cc. of dry pyridine and 2.5 gm. of trityl chloride added to the solution. The trityl chloride dissolved rapidly without any appreciable generation of heat. The mixture was heated to about 70° C. in a water bath for 15 min. and then allowed to stand for 48 hr. at room temperature. It was poured on to cracked ice, the precipitate filtered, washed with water and dried in a desiccator over sulphuric acid. The product was then dissolved in dioxane and the solution added, drop by drop, to dry ether, with vigorous stirring. The fine, powdery product was centrifuged, washed with fresh ether, again dissolved in dioxane and reprecipitated with ether. After centrifuging, washing with ether and petroleum ether, the product was dried at 100° C./2 mm. Yield, 4 gm. Found: OCH_3 , 8.4, 8.6; corr. 8.0, 8.2%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_5(\text{OCH}_2\text{CH}_2\text{OC}(\text{C}_6\text{H}_5)_3)(\text{OC}(\text{C}_6\text{H}_5)_3)(\text{OH})$, [1888.5]: OCH_3 , 8.2%.

Acetylation of the Previous Product

Trityl glycol lignin (2 gm.) was acetylated with pyridine and acetic anhydride and worked up as usual. Yield, 22 gm. It was purified by dissolving it in dioxane and pouring the solution into dry ether. The fine light-brown powder that was precipitated was centrifuged and washed with ether and petroleum ether. Found: OCH_3 , 8.3, 8.3; corr., 7.9, 7.9%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_5(\text{OCH}_2\text{CH}_2\text{OC}(\text{C}_6\text{H}_5)_3)(\text{OC}(\text{C}_6\text{H}_5)_3)(\text{OCOCH}_3)$, [1930.5]: OCH_3 , 8.0%.

Preparation of the Trityl Derivative of Glycol Lignin Premethylated with Diazomethane

Glycol lignin (1 gm.), premethylated with diazomethane, was treated with trityl chloride (2 gm.) in pyridine solution and worked up in the same way as that described for the original glycol lignin. Yield, 1.9 gm. Found: OCH_3 , 11.4, 11.2%; corr., 10.9, 10.7%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_6(\text{OCH}_2\text{CH}_2\text{OC}(\text{C}_6\text{H}_5)_3)(\text{OC}(\text{C}_6\text{H}_5)_2)(\text{OH})$, [1659.4]: OCH_3 , 11.2%.

Acetylation of the Previous Product

A portion (0.5 gm.) of the product obtained in the previous experiment was acetylated with pyridine and worked up in the usual manner. Found: OCH_3 , 10.6, 10.6; corr., 10.2, 10.2%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_6(\text{OCH}_2\text{CH}_2\text{OC}(\text{C}_6\text{H}_5)_3)(\text{OC}(\text{C}_6\text{H}_5)_2)(\text{OCOCH}_3)$, [1701.4]: OCH_3 , 10.9%.

Attempted Demethylation of Glycol Lignin with Hydrobromic Acid

Acetylated diazomethane-premethylated glycol lignin (0.5 gm.; OCH_3 , 17%) was dissolved in a mixture of 5 cc. of acetic anhydride and 5 cc. of glacial acetic acid saturated with hydrobromic acid. The solution was heated in a sealed tube for two hours at 120°C . then poured on to ice, the dark brown precipitate filtered, washed with water and dried over sodium hydroxide and phosphorus pentoxide. For the analysis the product was dried in an Abderhalden at $78^\circ\text{C}/2\text{ mm}$. Found: OCH_3 , 10.7%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_4(\text{OCOCH}_3)_5(\text{OCH}_2\text{CH}_2\text{OCOCH}_3)$, [1154.5]: OCH_3 , 10.7%. The product was free from bromine.

Numerous other experiments were carried out, but with little success.

References

1. BRAUNS, F. and HIBBERT, H. J. Am. Chem. Soc. 55 : 4720-4727. 1933.
2. GABRIEL, H. Dissertation. Leipzig. 1928.
3. HIBBERT, H. and MARION, L. Can. J. Research, 2 : 364-375. 1930.
4. HIBBERT, H. and ROWLEY, H. J. Can. J. Research, 2 : 357-363. 1930.
5. RASSOW, B. and GABRIEL, H. Cellulosechemie, 12 : 227-235; 249-254; 290-295; 318-320. 1931.
6. SCHORGER, A. W. The chemistry of cellulose and wood. McGraw-Hill Book Company, New York. 1928.
7. WAGNER, K. Dissertation. Leipzig. 1929.

STUDIES ON LIGNIN AND RELATED COMPOUNDS

XIV. THE ACTION OF LEAD TETRA-ACETATE AND OF MERCURIC ACETATE ON GLYCOL LIGNIN DERIVATIVES¹

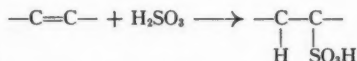
(PRELIMINARY COMMUNICATION)

BY K. R. GRAY², FRITZ BRAUNS³ AND HAROLD HIBBERT⁴

Abstract

Fully methylated glycol lignin (OCH₃, 30.4%) was treated with lead tetraacetate and with mercuric acetate. In the first case the acetoxyl group was introduced to the extent of 11.5%. With mercuric acetate in alcohol, the sole reaction was the substitution of hydrogen by the —HgOCOCH₃ group, there being no addition of ethoxyl nor loss of methoxyl groups. After repeated mercurization the final product contained 42.7% of mercury, that is, a ratio of introduced mercury atoms to original methoxyl groups of 1 : 1.

The presence of ethylenic bonds in lignin has not been definitely established. To account for the formation of a stable lignin sulphonic acid Klason (22, 23, 24) assumed that a double bond is present and that addition takes place to it as follows:



If the addition took place to a carbonyl group there would result an unstable sulphonic acid (21) from which sulphurous acid could be split off readily. Actually it is found that the greater part of the sulphur is firmly bound, apparently in the form of a stable sulphonic acid. The formation of a sulphonic acid does not definitely prove the presence of an ethylene bond, for there are other possibilities such as the sulphonation of a benzene nucleus (25), or the addition to a double bond formed during the reaction by the splitting off of water (10, p. 128).

The fact that gaseous chlorine, in the absence of moisture, has no appreciable action on wood, or on lignin, even at 80° C. is fairly good evidence of the absence of double bonds. On the other hand, Baur (2, 3, 4) has shown that many unsaturated compounds in which the double bonds are conjugated with benzene nuclei do not add halogen or only very slowly.

Many of the workers (5, 17, 19) who have obtained halogen derivatives of lignin have used aqueous or moist gaseous halogens, that is, they have employed conditions which favor oxidation and substitution rather than addition. Other workers (14, 15) have used solutions of dry halogens in non-aqueous solvents, but in nearly all cases have not distinguished between

¹ Manuscript received March 21, 1935.

Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Canada, with financial assistance from the Canadian Pulp and Paper Association. From a thesis presented by K. R. Gray, in October 1934, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Holder of a bursary under the National Research Council of Canada, 1931–32. Demonstrator, Department of Chemistry, McGill University, 1932–34.

³ Research Chemist and holder of Canadian Pulp and Paper Association Fellowship.

⁴ Professor of Industrial and Cellulose Chemistry, McGill University.

substitution and addition. Thus the results of the halogenation experiments are, in general, meaningless as regards the determination of ethylenic linkages in lignin.

A similar uncertainty exists regarding the question whether or not the nucleus of the lignin molecule is of an aromatic nature. It has been established that small amounts of aromatic compounds are formed on fusion with alkali, or on dry distillation, but this is not a certain proof of the presence of an aromatic nucleus since, in reactions of this kind, hydro-aromatic or even aliphatic compounds could easily be converted to aromatic derivatives by oxidation and loss of water. Moreover, since the amount of aromatic constituents isolated is usually small (less than 10%), these reactions convey relatively little enlightenment regarding the nature of the greater part of the lignin molecule.

Brauns and Hibbert (6, 7) have shown that native lignin with a "building unit" having a molecular weight of about 872 contains five hydroxyl groups, one of which can be methylated with diazomethane. This is supporting evidence for the presence of a phenolic hydroxyl group, although the reaction could also be given by an enolic hydroxyl group, as well as certain other derivatives, for example kojic acid (1) and ascorbic acid (18).

The usual methods for the determination of the structure of aromatic compounds have failed when applied to lignin. With halogenation, the results are complicated by partial loss of methoxyl groups (11, 13) and, if moisture is present, also by oxidation changes. Lignin is readily nitrated but simple derivatives are not obtained, owing to the fact that lignin is so readily oxidized and also because the introduced nitrogen is in the form of ester nitrogen (NO_3), nitrosonitrogen (NO), as well as in the form of nitro (NO_2) groups (20).

Since the classical structural methods have, over a long period of years, yielded only questionable information regarding the unsaturation, both ethylenic and aromatic, it would appear that further enlightenment must come through the application of new reagents.

The use of lead tetra-acetate as a reagent for the determination of unsaturated linkages in lignin was first investigated by Freudenberg and co-workers (11). They obtained from "Freudenberg lignin" a derivative with an acetyl content of 5.7%, corresponding to the addition of 7.8% acetoxy, or to one ethylenic linkage per eight methoxyl groups. Freudenberg (10, p. 127) has, however, suggested that double bonds may not actually exist in lignin, but that they may be formed by splitting off water, prior to addition taking place.

In the present investigation the action of lead tetra-acetate on glycol lignin was investigated and, in order to eliminate the possibility of the formation of double bonds, completely methylated glycol lignin (OCH_3 , 31.35%; corrected for glycol, 30.4%) was used. After heating the latter in dioxane solution for five hours with lead tetra-acetate the isolated product had an acetyl content of 7.45%, a methoxyl content of 24.85% (uncorrected) and

it contained lead also. The lead was removed by allowing the product to stand in a mixture of acetic anhydride and pyridine for one day. After purification, analyses showed an acetyl content of 8.35%, and a methoxyl content of 26.7%, uncorrected, or 25.9%, corrected for the effect of glycol.

Since the reaction was not repeated owing to lack of material, it cannot be decided whether the reaction was complete. Therefore no conclusions can be drawn regarding the ratio of acetoxyl introduced to methoxyl content.

However, since lead tetra-acetate is capable of replacing labile hydrogen atoms by acetoxyl groups (9), and very little is known regarding the structure of the lignin molecule and the presence or absence of such labile atoms, no definite conclusion at the moment can be reached in this matter.

Mercuric acetate, employed according to the method of Dimroth (8, 9), is one of the best reagents for indicating the presence of an aromatic ring structure. Under its influence the mercuri-acetoxyl ($-\text{HgOOCH}_3$) group is introduced into the ring.

Freudenberg (11) was the first to use this reagent in connection with lignin investigations. Treatment of a partially methylated Freudenberg lignin (OCH_3 , 28%) yielded a product containing 33% of mercury. The original material, as well as the derivative so obtained, was insoluble in all solvents. The latter substance had a methoxyl value of 13.8% as compared with a theoretical value of 16.0% calculated on the assumption that the only reaction taking place was the replacement of hydrogen in the nucleus by the mercuri-acetoxyl radical.

In the present investigation conditions were more favorable inasmuch as both the original lignin product and its reaction product were soluble in organic solvents, thus enabling the reaction to be carried out in a homogeneous solution. Under these conditions the completely methylated glycol lignin (OCH_3 , 31.35%; corrected for glycol, 30.4%) yields a mercuri-acetoxyl derivative, in which the methoxyl contents throughout the course of the reaction are seen (Fig. 1) to be in close agreement with the theoretical values based on the assumption that the sole reaction is the substitution of hydrogen by mercuri-acetoxyl groups.

Despite the fact that the reaction was carried out in homogeneous solution, the rate was much slower than that found by Freudenberg. This may be due to the fact that Freudenberg used an incompletely methylated lignin. In Fig. 1 curves are shown for two mercurization experiments. In Experiment 1 the mercuric acetate was renewed frequently during the initial period when the rate of reaction was greatest. In Experiment 2 the mercuric acetate was not renewed during the first 15 hr., with the result that the reaction took place more slowly.

Repeated mercurization yields a product with a final mercury content of 42.7% and a corrected methoxyl content* of 13.52%. (The actual OCH_3 value was 13.92%.) On the basis of a molecular weight of 986.5 (6, 16)

*Corrected for the influence of glycol on the methoxyl determination (16).

for fully methylated glycol lignin, the introduction of five mercuri-acetoxyl groups would require a mercury content of 43.8% and a methoxyl value of 13.6%.

The presence of aromatic rings, or of heterocyclic ring derivatives capable of functioning in an analogous manner, is thus indicated. If the reaction is due to the presence of benzene rings, five of these would be indicated, since, with aromatic compounds containing no free hydroxyl groups, the general action of mercuric acetate in alcohol is to introduce only one atom of mercury into an individual ring.

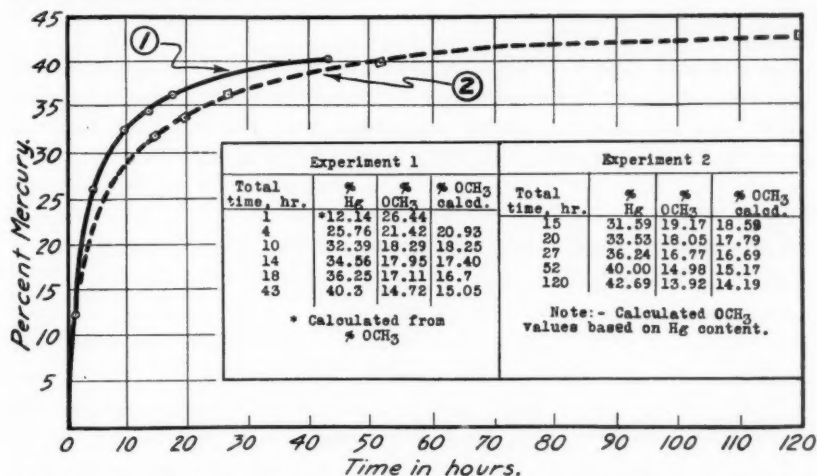
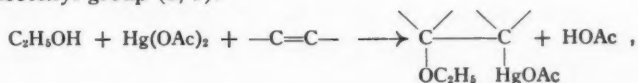


FIG. 1. Mercurization of fully methylated glycol lignin (the mercuric acetate was renewed after each analysis).

In the case of furane rings such a generalization cannot be made. The mercurization of these compounds has not been studied as closely as with aromatic compounds, but the available data show that the number of mercury atoms that can be introduced varies markedly with the nature of the substituent.

Since a molecular weight of 916 for the original glycol lignin corresponds to a unit containing five methoxyl groups, the ratio of the number of mercury atoms introduced to the number of original methoxyl groups is nearly 1 : 1, independently of the size of the formula adopted. Freudenberg found only 0.8 atoms of mercury per original methoxyl group (12).

The results of the mercurization experiments also indicate the absence of reactive ethylenic linkages. With an ethylenic linkage the typical reaction of mercuric acetate in absolute ethyl alcohol is the addition of an ethoxyl and a mercuri-acetoxyl group (8, 9).



while actually, in the mercurization of methylated glycol lignin, all the methoxyl values found are in close agreement with the assumption that no ethoxyl has been introduced, the only reaction taking place representing a substitution of nuclear hydrogen by —HgOAc groups.

This is the first known case of a substitution reaction for lignin not involving loss of methoxyl. The reaction would appear to be valuable for structural purposes for the following reasons: (a) there is no loss of methoxyl groups; (b) the product formed is soluble in organic solvents; (c) the number of atoms of mercury introduced bears a simple stoichiometrical relation to the number of methoxyl groups present.

It would seem that very definite and reliable structural information should be yielded by (i) an investigation of the reactions of the fully mercurized product, and (ii) a study of the mercurization of compounds the known structures of which are thought to be similar to that of lignin.

Experimental

Treatment of Fully Methylated Glycol Lignin with Lead Tetra-acetate.

Fully methylated glycol lignin (0.5 gm.; OCH_3 , 31.35%; corrected, 30.4%) was dissolved in 5 cc. of dry dioxane, and mixed with 1.8 gm. of lead tetra-acetate dissolved in 20 cc. of the same solvent. The mixture, protected from moisture, was heated at 50°C . for five hours. After cooling, and centrifuging, the small residue, apparently a mixture of lead acetate and lead dioxide was extracted with dioxane. The combined solutions were poured into 300 cc. of ice-water containing 30 cc. of glacial acetic acid, and the precipitated product centrifuged, washed in the centrifuge tube twice with 10% acetic acid, then three times with distilled water and dried. Yield, 0.65 gm.

The crude, dry product was dissolved in 5 cc. of dry benzene, the solution (about 7 cc.) filtered and added dropwise to 70 cc. of well stirred dry ether. The precipitate was centrifuged, washed in the centrifuge tube three times with ether, twice with petroleum ether (b.p. $30\text{--}50^\circ\text{C}$.), and dried, yielding a buff-colored powder having a somewhat more brownish tint than the original material. Yield, 0.50 gm. Found: Acetyl, 7.45%. (Acetoxyl, 10.20%). The product contained lead.

In order to remove this, the substance was dissolved in a mixture of pyridine and acetic anhydride, and after the solution had stood for 24 hr. at room temperature it was poured on to cracked ice, dried and purified as before. The ash content was then only 0.20%.

Analysis (corrected for ash-free product):— Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_9$ ($\text{OCH}_2\text{CH}_2\text{OCH}_3$)(OCOCH_3)₂ [1104.5]: OCH_3 , 28.0%; CH_3CO , 7.8%; (OCOCH_3), 10.7%. Found:— OCH_3 , 26.7, 26.7; corr. 25.9; CH_3CO , 8.3; OCOCH_3 , 11.4%.

The Mercurization of Fully Methylated Glycol Lignin

Two lots of fully methylated glycol lignin (OCH_3 , 31.35%; corrected, 30.4%) were subjected to repeated mercurization, following the procedure and purification described for the first mercurization. The methoxyl and mercury values obtained after each treatment are given in the Table in Fig. 1.

Methylated glycol lignin (1.0 gm.) was dissolved in a warm mixture of 10 cc. of absolute alcohol and 1 cc. of dioxane. Mercuric acetate (3 gm.) (Kahlbaum) was dissolved in a mixture of 30 cc. of absolute alcohol and 1.5 cc. of glacial acetic acid (the latter being added to prevent hydrolysis), the hot solution filtered and added to the solution of the methylated lignin. The mixture was refluxed on a water bath for 60 min. On cooling, some lignin material separated out. This was redissolved by adding about 5 cc. of dioxane; the solution was filtered to remove a small amount of inorganic salt, and the clear solution then added dropwise to 350 cc. of 2% acetic acid stirred mechanically. The precipitated mercurized methylated lignin was separated by centrifuging, washed five times by stirring with 1% acetic acid and then centrifuged. The last two washings on testing showed no trace of mercury. The mercurized product was dried to constant weight in a vacuum desiccator over sulphuric acid and sodium hydroxide. It was a fawn-colored powder. Yield, 1.35 gm.

The crude, dry product was purified by dissolving in 7 cc. of dioxane, filtering through a small Black Ribbon filter (Schleicher and Schüll), and the combined solution and washings (10 cc.) were added dropwise to 100 cc. of ether stirred mechanically. The precipitate was washed three times by stirring with ether, and centrifuging, and then twice in a similar way using petroleum ether (30–50° C.). The precipitate was allowed to stand overnight in the petroleum ether used for the final washing. The product was dried in a vacuum desiccator over sulphuric acid and sodium hydroxide. It was a fawn-colored powder. Yield, 1.1 gm. Analysis of the final product:—Calcd. for $\text{C}_{42}\text{H}_{27}\text{O}_6(\text{OCH}_3)_9(\text{OCH}_2\text{CH}_2\text{OCH}_3)(\text{HgOCOCH}_3)_5$ (2279.6): OCH_3 , 13.9%; Hg, 43.8%; CH_3CO , 9.4%. Found: OCH_3 , 13.9, 14.0% (corrected, 13.5, 13.6%); Hg, 42.7%; CH_3CO , 8.4%.

References

1. ARMIT, J. W. and NOLAN, T. J. *J. Chem. Soc.* 131 : 3023-3031. 1931.
2. BAUER, H. *Ber.* 37 : 3317-3321. 1904.
3. BAUER, H. and DIETERLE, H. *Ber.* 44 : 2691-2697. 1911.
4. BAUER, H. and MOSER, H. *Ber.* 40 : 918-924. 1907.
5. BEVAN, E. J. and CROSS, C. F. *J. Chem. Soc.* 38 : 666-669. 1880.
6. BRAUNS, F. and HIBBERT, H. *Pulp & Paper Mag. Can.* 34 : 187-188. 1933.
7. BRAUNS, F. and HIBBERT, H. *Can. J. Research, B*, 13 : 28-34. 1935.
8. DIMROTH, O. *Ber.* 35 : 2853-2873. 1902.
9. DIMROTH, O. and SCHWEIZER, R. *Ber.* 56 : 1375-1385. 1923.
10. FREUDENBERG, K. *Tannin, Cellulose, Lignin.* J. Springer. Berlin. 1933.
11. FREUDENBERG, K., BELZ, W. and NIEMANN, C. *Ber.* 62 : 1554-1561. 1929.
12. FREUDENBERG, K., SOHNS, F., DÜRR, W. and NIEMANN, C. *Cellulosechemie*, 12 : 263-276. 1931.

13. FRIEDRICH, A. and PELIKAN, E. *Biochem. Z.* 239 : 461-472. 1931.
14. FUCHS, W. *Brenstoff-Chem.* 9 : 348-350. 1928.
15. FUCHS, W. and HORN, O. *Ber.* 61 : 2197-2202. 1928.
16. GRAY, K. R., KING, E. G., BRAUNS, F. and HIBBERT, H. *Can. J. Research, B*, 13 : 35-47. 1935.
17. HÄGGLUND, E. *Arkiv Kemi, Mineral. Geol.* 7 : 15. 1918.
18. HERBERT, R. W., HIRST, E. L., PERCIVAL, E. G. V., REYNOLDS, R. J. W. and SMITH, F. *J. Chem. Soc.* 133 : 1270-1290. 1933.
19. HEUSER, E. and SIEBER, R. *Z. angew. Chem.* 26, I : 801-806. 1913.
20. HIBBERT, H. and MARION, L. *Can. J. Research*, 3 : 130-139. 1930.
21. HOOVER, G. I., HUNTEN, K. W. and SANKEY, C. A. *J. Phys. Chem.* 34 : 1361-1386. 1930.
22. KLASON, P. *Ber.* 53 : 706-711. 1920.
23. KLASON, P. *Ber.* 53 : 1862-1863. 1920.
24. KLASON, P. *Ber.* 53 : 1864-1873. 1920.
25. LAUER, W. M. and LANGKAMMERER, C. M. *J. Am. Chem. Soc.* 56 : 1628-1629. 1934.

STUDIES ON LIGNIN AND RELATED COMPOUNDS

XV. PHENOL GLYCOL LIGNIN¹

BY FRITZ BRAUNS² AND HAROLD HIBBERT³

Abstract

Phenol condensation products of glycol lignin, of a premethylated and a fully methylated glycol lignin have been prepared. In each case it has been found that, on the basis of the five methoxyl groups present in the original glycol lignin, three molecules of phenol react with one lignin unit by nuclear condensation, and when the product is worked up immediately no loss of methoxyl groups occurs. With the fully methylated glycol lignin in one experiment, some of the methoxyl groups were removed but the hydroxyl groups thus formed could not be remethylated with diazomethane, thus indicating their probable aliphatic character. Quercetin does not give a phenol condensation product under the same conditions.

Introduction

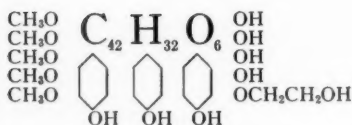
As shown in the following paper (2) lignin can be extracted from wood meal by heating with phenol at a low temperature in the presence of dry hydrogen chloride as catalyst, yielding the so-called "phenol lignin". The structure of this compound and the mechanism of its formation are still unknown, in spite of the number of recent investigations (4, 6) carried out on the subject. It was pointed out previously (1) that in this reaction one phenol molecule reacts with the lignin to form a compound having an ether linkage, and three other phenol molecules react stoichiometrically with a lignin unit containing five methoxyl groups. Additional proof of this is now provided in the experimental results described in this paper. When glycol lignin is heated with phenol in the presence of a trace of hydrochloric acid, the color of the phenol lignin solution changes immediately from a reddish- to a violet-brown. The isolated and purified phenol glycol lignin (Formula I) has a methoxyl content of 13.1%, that of the original product being 16.9%. This decrease corresponds exactly with the entrance of three phenol groups into a lignin molecule having the structure $C_{42}H_{32}O_6(OCH_3)_5(OH)_4.(OCH_2CH_2OH).3C_6H_5OH$. In glycol lignin the hydroxyl group capable of etherification by means of alcohol and hydrochloric acid has been replaced by a glycol group, and the three phenol molecules must therefore have all undergone nuclear condensation, thus introducing three new free phenolic hydroxyl groups. This is shown by the methylation experiments with diazomethane, as well as by the results obtained on benzylation. Methylation with diazomethane indicates that, in addition to the probable presence of one phenolic hydroxyl group in the original glycol lignin, there are present three new phenolic hydroxyl groups originating from the three newly entering phenol molecules.

¹ Manuscript received March 21, 1935.

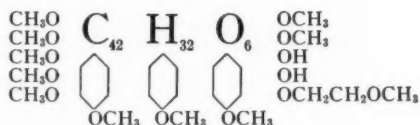
Contribution from the Division of Industrial and Cellulose Chemistry, Pulp and Paper Research Institute, McGill University, Montreal, Canada, with financial assistance from the Canadian Pulp and Paper Association.

² Research Chemist and holder of Canadian Pulp and Paper Association Fellowship.

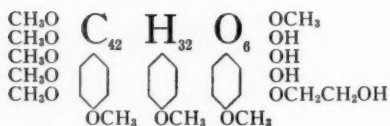
³ Professor of Industrial and Cellulose Chemistry, McGill University.



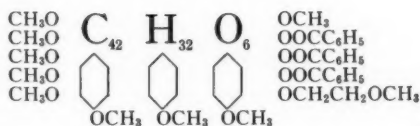
I



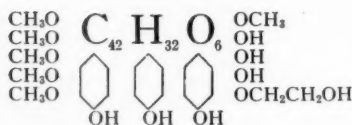
V



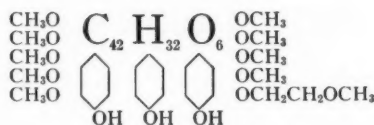
II



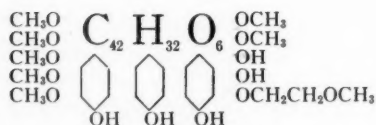
VI



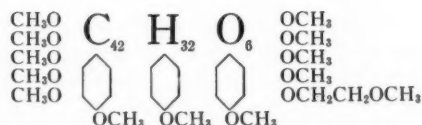
III



VII



IV



VIII

The presence of other free non-phenolic hydroxyl groups is indicated by the formation of an acetyl derivative on acetylation of the diazomethane-methylated product. The values calculated from the formulas adopted in the experimental part are based on the formula for glycol lignin derived in an earlier paper (1).

Diazomethane-methylated glycol lignin was treated with phenol in a similar manner, and here also it was found that, with each lignin unit containing six methoxyl groups present in the diazomethane-methylated glycol lignin, three phenol molecules react to give a phenol condensation product containing three (new) phenolic hydroxyl groups, as shown by formation, on benzylation, of a benzoylated phenol methyl glycol lignin containing seven benzoyl groups.

Finally it was of interest to ascertain whether the remaining three free hydroxyl groups in glycol lignin play any part in the condensation reaction with phenol. Fully methylated glycol lignin (OCH_3 , 31.5%) was therefore condensed with phenol in the usual manner. In the first experiment the reaction product was not purified immediately, and it was found later, from the analytical data, that approximately two methoxyl groups had been split off, a fact confirmed by the subsequent methylation experiment with diazomethane in which the three new phenolic hydroxyl groups were methylated

(Formula V). On benzoylation of the latter product in pyridine solution with benzoyl chloride another methoxyl group was removed and substituted by a benzoyl group as shown by analysis. This was also confirmed by the strong smell of methyl benzoate in the precipitated product. For a compound containing eleven methoxyl and two benzoyl groups, the calculated methoxyl value is 22.9%; for one containing ten methoxyl and three benzoyl groups the calculated methoxyl value is 19.6%. The latter value agrees very well with that found. In a second experiment, in which the product was worked up immediately, a phenol glycol derivative was obtained which still contained all the original methoxyl groups.

In recent publications (3, p. 136; 5) the suggestion has been made that lignin contains oxygen rings of the catechin, pyrone or flavone types. It seemed of interest, therefore, to examine the behavior of quercetin towards phenol and anhydrous hydrogen chloride under the same conditions as those used in the preparation of phenol lignin. No condensation was found to occur, thus indicating that the reaction with phenol is due to the presence of groupings other than those of a flavone type.

Experimental

Action of Phenol on Glycol Lignin

Glycol lignin (2 gm.) was dissolved in phenol (25 gm.), the solution heated on the water bath to 80° C., and 5 cc. of an ether solution containing 5% anhydrous hydrogen chloride added. The reddish-brown solution immediately turned a violet-brown. This solution was heated for 10 min., and an additional 2 cc. of the ether-hydrogen chloride solution was added. Heating was then continued for 10 min., and the same amount of the ether-hydrogen chloride solution was again added. After heating for a further period of 10 min. the phenol was distilled off as much as possible under reduced pressure at a temperature not over 85° C. The residue was dissolved in methyl alcohol and the solution poured into distilled water, the powdery precipitate filtered, washed with water and dried in a desiccator over sodium hydroxide and sulphuric acid. Yield of crude phenol compound, 2.8 gm. It was dissolved in dioxane, the solution centrifuged and filtered, and the product precipitated by adding the solution dropwise to dry ether, and stirring vigorously. It separated out as a fine light-violet-brownish powder, which was washed twice with ether, then three times with petroleum ether, dried and analyzed. Found: OCH_3 , 13.1%*. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_5(\text{OH})_4(\text{OCH}_2\text{CH}_2\text{OH}) \cdot 3\text{C}_6\text{H}_5\text{OH}$, [1198.6] (Formula I): OCH_3 , 13.0%.

Repeated phenolation brought about no change in composition. The phenol glycol lignin is soluble in dioxane, acetone, pyridine, dilute sodium hydroxide solution, insoluble in benzene, ether, petroleum ether and water.

In a second experiment 7 gm. of glycol lignin was phenolated in the same manner. Yield after two phenolations, 7.5 gm. Found, OCH_3 , 13.5%.

*No correction has been applied for the slight increase in value due to the presence of the glycol radical, as this falls well outside the limit of experimental error for the products in question.

Methylation of Phenol Glycol Lignin with Diazomethane

Phenol glycol lignin (Formula I) (2 gm.; OCH_3 , 13.5%) was twice methylated and was then found to be no longer acted upon by the methylating reagent. Found: OCH_3 , 23.1%. Analysis after a third methylation:—Found: OCH_3 , 23.2%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_6(\text{OH})_3\text{OCH}_2\text{CH}_2\text{OH}$. $3\text{C}_6\text{H}_5\text{OCH}_3$, [1254.6] (Formula II): OCH_3 , 22.3%.

Acetylation of Phenol Glycol Lignin Premethylated with Diazomethane

Diazomethane-methylated phenol glycol lignin (1.3 gm.) was dissolved in dry pyridine (15 cc.). Acetic anhydride (10 cc.) was added, and the mixture allowed to stand at room temperature for 40 hr. It was poured on to ice, the precipitated product filtered and purified by precipitating from dioxane solution into ether. Found: OCH_3 , 21.2%.

Benzoylation of Phenol Glycol Lignin

Phenol glycol lignin (1 gm.) was benzoylated using 10 cc. of pyridine and 3 gm. of benzoyl chloride at room temperature. After 48 hr. the mixture was poured on to ice and the solution extracted with chloroform. The chloroform solution was washed successively with dilute sulphuric acid, water, potassium bicarbonate solution, and water, and was finally dried with magnesium sulphate. The product was precipitated by pouring the chloroform solution into dry ether, from which it separated out as a fine, dry, brown powder. Found: OCH_3 , 7.5%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_5(\text{OCOC}_6\text{H}_5)_4(\text{OCH}_2\text{CH}_2\text{OCOC}_6\text{H}_5)$. $3\text{C}_6\text{H}_5\text{OCOC}_6\text{H}_5$, [2030.8]: OCH_3 , 7.6%.

Phenol Compound of Glycol Lignin Premethylated with Diazomethane

Glycol lignin (2 gm.) was premethylated with diazomethane and then phenolated in the same manner as that used with glycol lignin and the crude product (2.5 gm.) purified, using dioxane and ether. The dioxane ether solution was completely colorless. Found: OCH_3 , 16.1%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_6(\text{OH})_3\text{OCH}_2\text{CH}_2\text{OH}$. $3\text{C}_6\text{H}_5\text{OH}$, [1212.6]: OCH_3 , 15.4%. The product has the same solubility relations as the corresponding glycol lignin derivative.

Benzoylation of the Phenol Derivative of Glycol Lignin Premethylated with Diazomethane

The above-mentioned phenol derivative of the premethylated glycol lignin (1 gm.) was benzoylated and purified as described above for the benzoylated phenol glycol lignin. Yield, 1.1 gm. Found: OCH_3 , 9.5%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_6(\text{OOC}_6\text{H}_5)_3(\text{OCH}_2\text{CH}_2\text{OOC}_6\text{H}_5)$. $3\text{C}_6\text{H}_5\text{OOC}_6\text{H}_5$, [1940.9]: OCH_3 , 9.6%. The product is a finely divided, light-brown powder, soluble in dioxane, acetone, pyridine, glacial acetic acid, and insoluble in ether, petroleum ether, water and dilute sodium hydroxide.

*Phenol Derivative of Fully Methylated Glycol Lignin**Experiment I*

Fully methylated glycol lignin (2.5 gm.) was dissolved in 25 gm. of phenol and the solution heated to 80° C., and 2 cc. dry ether containing 2.5% anhydrous hydrogen chloride added. After 10 min., 0.5 cc. of the ether-hydrogen chloride solution was added and the same amount again after a further 10 min. After heating for 30 min. in all, since the mixture could not be worked up the same day, it was allowed to stand overnight. The phenol was then distilled off, the residue dissolved in a mixture of methyl alcohol and acetone (1 : 1) and the product precipitated by pouring the solution into distilled water. The crude product (2.8 gm.) was purified from dioxane and ether. Found: OCH_3 , 20.5%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_9(\text{OCH}_2\text{CH}_2\text{OCH}_3) \cdot 3\text{C}_6\text{H}_5\text{OH}$, [1268.6]: OCH_3 , 24.45%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_7(\text{OH})_2(\text{OCH}_2\text{CH}_2\text{OCH}_3) \cdot 3\text{C}_6\text{H}_5\text{OH}$, [1240.6] (Formula IV): OCH_3 , 20.1%. This value is in agreement with the assumption of a loss of two methoxyl groups during the phenolation.

The product was then methylated with diazomethane. The above-mentioned phenol compound of fully methylated glycol lignin (1.75 gm.) was methylated repeatedly in dioxane solution with diazomethane and the product purified, using dioxane and ether. Prior to analysis it was washed twice with ether, three times with petroleum ether and dried. Yield, 1.8 gm. Found: OCH_3 , 26.7%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_7(\text{OH})_2 \cdot \text{OCH}_2\text{CH}_2\text{OCH}_3 \cdot 3\text{C}_6\text{H}_5\text{OCH}_3$, [1282.7] (Formula V): OCH_3 , 26.6%.

A portion (0.7 gm.) of the diazomethane-methylated product was benzoylated by dissolving it in a mixture of 6 cc. pyridine and 3 cc. of benzoyl chloride. After it had stood for 48 hr. at room temperature, the product was poured on to cracked ice. A sticky mass separated out which smelled strongly of methyl benzoate and did not solidify even after washing with water. On mixing with ether the product solidified, and the powdery product was filtered, dried, and purified from dioxane and ether. Yield, 1 gm. Found: OCH_3 , 19.6%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_7(\text{OOC}\text{C}_6\text{H}_5)_2 \cdot \text{OCH}_2\text{CH}_2\text{OCH}_3 \cdot 3\text{C}_6\text{H}_5\text{OCH}_3$, [1490.6]: OCH_3 , 22.9%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_6(\text{OOC}\text{C}_6\text{H}_5)_3 \cdot \text{OCH}_2\text{CH}_2\text{OCH}_3 \cdot 3\text{C}_6\text{H}_5\text{OCH}_3$, [1580.7] (Formula VI): OCH_3 , 19.6%. The methoxyl value found is seen to be in good agreement with the assumption of the removal of one methoxyl group and its replacement by a benzoyl group together with benzoylation of the two free hydroxyl groups.

Experiment II

Fully methylated glycol lignin (2.5 gm.) was dissolved in 20 gm. of phenol, the solution heated to 80° C. and 1 cc. of dry ether containing 2.5% of hydrochloric acid added. The mixture was treated in the same manner as in Experiment I. After the reaction was finished, the excess of phenol was distilled off *immediately*, the residue dissolved in acetone and the reaction product precipitated by adding the solution dropwise to distilled water. The yellowish-brown precipitate was filtered and dried (yield, 3 gm.). It

was dissolved in 30 cc. of dioxane and precipitated in well stirred, dry ether. Found: OCH_3 , 24.1%. The methoxyl value did not change on repeating the phenolation, as shown by the following figures:—Found: OCH_3 , 24.5%. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_9(\text{OCH}_2\text{CH}_2\text{OCH}_3) \cdot 3\text{C}_6\text{H}_5\text{OH}$, [1268.6] (Formula VII): OCH_3 , 24.4%.

Methylation of Phenol Diazomethane-methylated Glycol Lignin (Formula III) with Dimethyl Sulphate and Sodium Hydroxide

The above-mentioned phenol diazomethane-methylated glycol lignin (3 gm.) was methylated further in acetone solution with dimethyl sulphate and sodium hydroxide (30%) at room temperature. After the first methylation the acetone solution was separated from the aqueous layer and the product remethylated in the same way. A sample was then isolated and purified. Found: OCH_3 , 29.9%.

This value did not change after treatment of the product with acetic anhydride and pyridine, indicating the absence of free hydroxyl groups. Yield, 3 gm. Calcd. for $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OCH}_3)_9\text{OCH}_2\text{CH}_2\text{OCH}_3 \cdot 3\text{C}_6\text{H}_5\text{OCH}_3$, [1310.7] (Formula VIII): OCH_3 , 30.7%.

Action of Phenol on Quercetin in Presence of Hydrochloric Acid

Quercetin (2 gm.) was suspended in 20 gm. of molten phenol, the mixture heated in a water bath to 85° C. and then 5 cc. of ether containing 0.03 gm. anhydrous hydrogen chloride added. The mixture was maintained for 10 min. at the same temperature and shaken frequently. A second 5 cc. of the ether-hydrogen chloride solution was then added, and the mixture heated for a further 10 min. This was followed by a third similar treatment, the total time of heating at 85° C. being 30 min. No such change in the color of the solution or of the quercetin took place as was observed in the case of the lignin derivatives. The phenol was distilled off under reduced pressure, the yellowish powdery residue washed with water and dried in a desiccator over sulphuric acid. Yield, 2 gm.; m.p., 310° C.; m.p. of quercetin, 312–313° C.; mixed m.p., 311° C. The quercetin was recovered unchanged.

References

1. BRAUNS, F. and HIBBERT, H. J. Am. Chem. Soc. 55 : 4720-4727. 1933.
2. BUCKLAND, K. I., BRAUNS, F. and HIBBERT, H. Can. J. Research, B, 13 : 61. 1935.
3. FREUDENBERG, K. Tannin, Cellulose, Lignin. J. Springer, Berlin. 1933.
4. HILLMER, A. Cellulosechemie, 6 : 169-187. 1925.
5. KLASON, P. Ber. 53 B : 1864-1873. 1920.
6. WEDEKIND, E., ENGEL, O., STORCH, K. and TAUBER, L. Cellulosechemie, 12 : 163-173. 1931.

